NPS ARCHIVE
1965
CHUMLEY, S.

SUEPERPLASTICITY IN AN ALUMINUM-ZINC ALLOY

SYLVESTER G. CHUMLEY
and
GEORGE R. MEINIG

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY, CA 93943-5101

U. S. NAVAL POSTGRADUATE SCHOOL
MONTEREY, CALIFORNIA

53

SUPERPLASTICITY
IN AN ALUMINUM - ZINC ALLOY

by

Sylvester G. Chumley

Lieutenant, United States Navy

and

George R. Meinig, Jr.

Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
MATERIALS SCIENCE

United States Naval Postgraduate School
Monterey, California

1 9 6 5

NPS ARCHIVE
1965
CHUMLEY, S.

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY, CA 93943-5101
Monterey, California

SUPERPLASTICITY
IN AN ALUMINUM - ZINC ALLOY

by

Sylvester G. Chumley

and

George R. Meinig, Jr.

This work is accepted as fulfilling

the thesis requirements for the degree of

MASTER OF SCIENCE

IN

MATERIALS SCIENCE

from the

United States Naval Postgraduate School

ABSTRACT

Recent investigations have demonstrated remarkable ductility in a 20 weight per cent Aluminum - 80 weight per cent Zinc alloy. An understanding of the mechanisms responsible for this superplastic behavior could have important applications in other commercial alloy systems.

This investigation consists of correlated metallographic examination, X-ray diffraction analysis, and tensile testing of Al-Zn binary alloys of 17 per cent, 20 percent, and 23 per cent Aluminum at specific stages of treatment.

Special attention is focused on the heat evolution which follows quenching, a phenomenon apparently associated with the spontaneous breakdown of the unstable α' structure. Of particular interest is the appearance of a disorganized, undefined structure after the heat evolution as evidenced by diffraction analysis. The subsequent organization of this structure and apparent diffusional effects as aging takes place at room temperature is clearly indicated by experimental evidence. The lack of three-dimensional periodicity in space following quenching from the single phase region suggests a strong analogy between the alloys studied and the viscous behavior of glass-like materials.

TABLE OF CONTENTS

Section	Title	Page
1.	Background	1
2.	Experimental Procedures	10
3.	Tensile Tests	13
4.	Heat Evolution	17
5.	Metallographic Observations	19
6.	Diffraction Analysis	24
7.	Discussion of Results	29
8.	Acknowledgements	31
9.	Bibliography	32
10.	Appendix I (Photomicrographs)	
11.	Appendix II (X-ray Diffractometer Patterns)	

LIST OF ILLUSTRATIONS

Figure		Page
1.	Al-Zn Phase Diagram.	2
2.	Sketch of tensile testing apparatus.	15
3.	Tensile specimens, as machined.	16
4.	Tensile specimens, before testing.	16a
5.	Tensile specimens, after testing.	16a
6.	Time-temperature plot of heat evolution.	18
7.	Photomicrographs.	Appendix I
8.	X-ray Diffractometer Patterns.	Appendix II

1. Background.

The phenomenon of "superplasticity" was first recognized by Sauveur when he discovered an unusual degree of plasticity in the presence of the alpha-gamma phase transformation while conducting experiments on mild steel. Investigation of this phenomenon was pursued by De Jong and Rathenau in 1959. Their basic technique involved cycling a specimen of pure iron or mild steel between selected temperatures within the two phase alpha-gamma region while under continual stress. Results indicated that the elongation was a linear function of the amount of material transformed in the alpha-gamma transformation, and that the elongation was a linear function of the applied stress.

Their findings showed a drastic decrease in the yield strength during the alpha-gamma phase change, and also indicated that reduction in yield strength is sensitive to the rate of phase change [1,2].

The phenomenon of unusual ductility in iron and mild steel is similar to that observed in Al-Zn and other alloy systems, but of much lesser magnitude. Common features of the alloy systems which may give rise to superplastic behavior are not presently understood, but intensive research is being carried out on specific alloys which may yield an insight into this type of behavior.

In 1944 two Soviet workers, Bochvar and Sviderskaia, began investigating a 20% Al - 80% Zn alloy.[1] They coined the term "superplasticity" in their 1945 paper, and the name has since been accepted into the metallurgical jargon. Their study stimulated interest in this alloy among

---

[1] All alloy compositions will be given in weight percent.

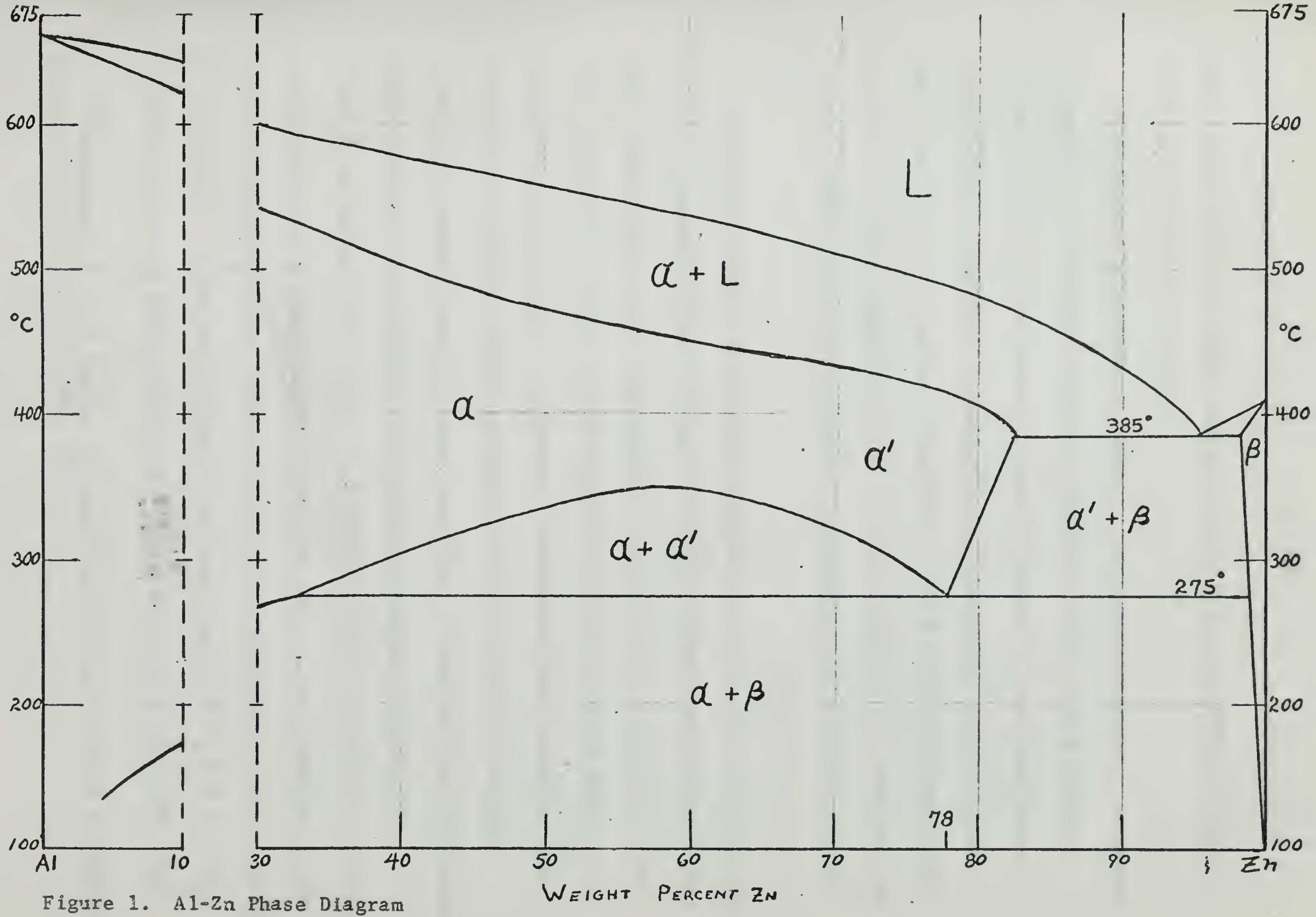


Figure 1. Al-Zn Phase Diagram

other Soviet workers, formost among whom has been Presnyakov, whose investigations date from 1958.

Presnyakov's experimental technique was straightforward. He heated his specimens to the single phase α' region at 375°C (see Figure 1), quenched them to the two phase α plus β region at room temperature, and subsequently reheated to temperatures between 200° and 300°C for tensile testing. He reported elongations of 650% without fracture when the tensile testing temperature was held just below 275°C. The test was limited to 650% elongation because of the physical size of his furnace [3].

Presnyakov noted that an alloy quenched from 375° had a larger value of lattice parameter than the same alloy cooled under equilibrium conditions, and concluded that the quenched alloy was in a metastable state which resulted from partial transformation of the α' single phase to the equilibrium α plus β structure. He observed that the alloy with the largest value of lattice parameter in the as quenched condition showed the greatest tendency toward superplastic behavior upon subsequent tensile testing. For example, the lattice parameter changed from 4.0414 Å in the metastable state to 4.0384 Å in the equilibrium condition in the case of the 650% elongation, whereas the lattice parameter of the metastable state was less than 4.0414 Å (but still greater than 4.0384 Å) in tests when the maximum elongation was less than 650%.[2] (It is interesting to note that these lattice parameters are not in agreement with

---

[2] Underwood, E. E. A Review of Superplasticity and Related Phenomena. Journal of Metals, v. 14, 1962: 914.

Ellwood reports [4]. However, the change in parameter is of more interest here than the actual value of the parameter itself.)

Presnyakov's findings can be summarized as follows:

(1) Quenching from below the eutectoid temperature (275°C) does not produce any subsequent superplastic effect;

(2) Superplasticity is observed when the quenching temperature is 275° or higher, and increases as the quenching temperature increases;

(3) Slowly cooled alloys do not display any special ductility.

He explained these observations by the presumptions that:

(a) Quenching must prevent decomposition to the equilibrium state - i.e., a metastable structure must be maintained for subsequent stressing. Also, the higher the quenching temperature, the greater the degree of metastability, and the greater the atomic mobility under stress;

(b) The greater the proportion of the alloy in the metastable state, the greater is the superplastic effect, since the volume of alloy to be transformed is greater [3].

Presnyakov and his coworkers also discovered similar, but less startling ductility in the Cu-Zn system and in the eutectic alloys of Al-Cu, Al-Si, Pb-Sn, Pb-Cd, Mg-Al, and Mg-Cu. All the systems except Cu-Zn showed superplastic behavior when heat treated in a manner analogous to the Al-Zn eutectoid. In the Cu-Zn alloy, the effect occurs in conjunction with the phase change induced by deformation in the alpha-beta and beta-gamma brasses, and an order-disorder reaction in the beta brasses.

An interesting result of the experiments was that ductility is greater in tensile testing than in impact testing for identical specimens.

This confirms earlier indications that the rate of deformation is an important consideration in the phenomenon of superplasticity. This could be expected since the effect must depend on the kinetics of atom mobility.

More recent work with the Al-Zn alloy has been carried out by Backofen at MIT, who used cast tensile specimens of 80±0.1% Zn - 20±0.1% Al prepared from Al and Zn of at least 99.9% purity. Prior to testing specimens, Backofen quenched from 375°C, reheated to about 250°, and let the specimens soak at this temperature for predetermined times before tensile loading.

The most dramatic results of this testing program were twofold. First, a tensile specimen was elongated 1000% before fracture. Subsequently a thin sheet of the alloy was bulged into a dome-like hemispherical shape by application of gas pressure [5] . Behavior in this manner is characteristic of a glass-like material, but not a metal. Consequently the need for an adequate model, or explanation, that could account for these ductility effects was apparent from the beginning of the studies.

De Jong attributed his observations on iron and mild steel to the following mechanism: when the density of the two phases concerned is different, the directing effect of applied stress on the deformations resulting from lattice adjustment during phase transformation may contribute to the elongation. He did note that there might be other processes which contribute to the effects [6].

Vorob'ev carried on studies parallel in most respects to those of De Jong and Rathenau. He determined that plasticity is higher during transformation than before or after, and that during sub-zero temperature

transformations to martensite, the rate of deformation is proportional to the amount of austenite transformed during the deformation. He concluded from this that diffusional processes are not necessary for enhanced ductility during some phase transformations, and suggested that instantaneous weakening of inter-atomic bonds during the phase transformation is a cause of the effect.[3]

Porter and Rosenthal devised a dislocation mechanism to account for the phenomena observed. They suggested that piled-up dislocations at grain boundaries and other barriers within the structure produce stress fields which result in increased rates of nucleation, to the end that, as the nucleus begins to grow, its expanding face acts as a sink for piled up dislocations, thus allowing the additional plastic deformation.[4]

Sherby and Clinard studied the effects of allotropic transformation on the plastic properties of high purity iron under various torsion and compression stresses through the alpha-gamma transformation. Their results indicated that transformation strain constitutes a significant portion of the total strain when heating or cooling at high stresses, while at lower stresses the normal creep becomes a relatively large factor. Also, transformation strain is a function of the rate of temperature change. It has a slightly greater than linear dependence on applied stress and it exhibits this dependence to a greater degree on heating than on cooling.

[3] Underwood, E. E. A Review of Superplasticity and Related Phenomena. Journal of Metals, v. 14, 1962: 918.

[4] Ibid.: 919.

The model they proposed to explain these findings is based on the volume change in going from one phase to the other - about 1% decrease in going from the alpha to the gamma phase - and the resultant (hypothesized) generation of vacancies and interstitials as the change is accomplished. When the volume decreases vacancies can be generated, and conversely when the volume increases, interstitials can be created.[5,6]

According to dislocation theory, the rate of dislocation climb is a function of the number of vacancies and interstitials present. Since plastic deformation is dependent on dislocation movement, and climb is an essential part of this movement, it follows that there is a direct connection between the number of interstitials and vacancies and the amount of plastic deformation of the specimen [7,8]. That the transformation strain is greater on heating than on cooling is explained by the fact that the alpha matrix on heating is inherently weaker than the gamma matrix on cooling, and hence more strain is observed. Also contributing is the generation of vacancies - aiding the climb mechanism - during heating.

In the case of the Al-Zn alloys, Soviet researchers hold that the application of stress at elevated temperatures can lead to profound changes in the structure of solid solutions. A stressed condition of the alloy promotes a rearrangement of the atoms, facilitating the processes of segregation, nucleation, and growth of new phases which

[5] Sherby, O. D. and A. Goldberg. Comments...Acta Met., v. 9, 1961: 510.

[6] Sherby, O. D. and F. W. Clinard. Strength of Iron During Allotropic Transformation. DMS Report 63-5, Stanford U., 1963.

are stable under the applied stress. The increased diffusion of atoms in the direction of the stress gradient reduces internal stresses and tends to restore the distorted lattice to an equilibrium condition. Then the lattice can presumably undergo further plastic deformation. In effect, they attempt to account for the extreme weakness of the material, since almost no stress is required to produce extreme elongations under the testing conditions. In contrast to this approach, Backofen attacks the problem by attempting to explain the mechanism which accounts for the glass-like behavior, hence the extreme ductility, which is accomplished in the absence of necking in the specimen.

He reasons that, in order to avoid necking, a strain induced hardening is required to offset the geometrical weakening caused by the reduction in cross section in the specimen. This hardening could have its origin in such mechanisms as metallurgical cold working, a local decrease in temperature, an increase in surface energy, or in an increase in strain rate. Of these Backofen selects the strain-rate hardening mechanism as being the most likely, and the one which best explains both his experimental data and the results of recent measurements by Presnyakov and Starikova involving strain-rate sensitivity of the phenomenon [5].

Sauerwald and Schulze suggest that the finely divided microstructure of quenched and transformed Al-Zn alloy is an important factor in strain-rate sensitivity because of the increased amount of grain boundary material thus introduced, which could deform in a viscous manner. That this could be pertinent can be illustrated by considering the flow

and elongation in hot glass, wherein the essentially unlimited elongation is a result of the direct proportionality between flow stress and strain rate; i.e., Newtonian viscosity [5].

2. Experimental.

Experimental procedures were developed in four distinct areas: melting and casting the alloys; machining and preparing specimens from the casting; design and construction of the tensile testing apparatus; and development of metallographic and X-ray diffractometer techniques.

Three alloys were selected for study in the Al-Zn system: 17% Al-83% Zn, 20% Al-80% Zn, 23% Al-77% Zn - all percentages by weight, ±.1%. Aluminum used was 99.992% pure. Two grades of zinc were used, one of 99.9% purity, the other of 99.999% purity-which was used for high purity specimens.

The eutectoid of interest in the Al-Zn system occurs at 22% Al-78% Zn, but Presnyakov showed that the optimum alloy for the superplastic effect is 20% Al-80% Zn. The three alloy compositions studied were chosen to bracket both the eutectoid and the optimum superplastic composition.

An induction furnace was used to melt the base metals in a cylindrical graphite crucible to obtain the alloys of desired composition. The aluminum was melted first due to its considerably higher melting temperature (660°C). The zinc was slowly added to the molten aluminum until the desired composition was obtained. During this process, the melt was maintained in a molten condition. To eliminate oxidation and to provide mechanical stirring of the molten alloys, a hollow carbon stirring rod was employed, through which was bled low pressure nitrogen. When entirely molten, and about 20°C above the liquidus temperature (480°C), the melt was poured into a preheated (375°C) zirconia boat and allowed to cool in air until solidified. To refine grain size and

[illegible]

[illegible]

[illegible]

homogenize the cast alloys, the castings were heated to 375°C for four hours, quenched in brine to room temperature, and immediately cold rolled to a reduction of 9%. The heat of evolution liberated subsequent to quenching under these conditions occurred just prior to and during cold rolling. The castings were then homogenized at 375°C between 20 and 30 hours, allowed to air cool to room temperature, and each prepared into three specimens - one for tensile testing, one for X-ray diffractometer use (lattice parameter determination), and the third for metallographic examination. This completed, the specimens were reheated to 375°C for 50 hours preparatory to the final testing procedures.

The tensile testing specimen was machined on a planer and a router to the dimensions illustrated in figure (2). The initial gage length was taken as 1.6 inches.

The X-ray diffractometer specimen was ground flat on a belt sander and polished with crocus cloth to obtain a strong X-ray reading. The metallographic specimen was handled without mounting to facilitate quenching during the testing phase. A one micron diamond wheel was used for the final polish, after which the specimen was etched by immersion at room temperature. The etchant developed for this alloy was a solution of Palmerton's reagent diluted 2 to 1 with distilled water, to which was added 5% by volume of 1% HF solution.

Evaluation of the plasticity of the specimens necessitated the evolvement of a controllable, constant strain-rate, tensile testing device. Figure (3) illustrates the resulting apparatus which fulfilled this requirement. It incorporated a 1/8 HP DC motor operating off a thyrotron control unit, which drove through a 1400 to 1 reduction gear

to a 2 to 1 sprocket reduction which provided power to a chain and sprocket drive. A second sprocket attached to the output shaft provided a power takeoff for the chain drive, carefully designed so that the travel of the two chains was exactly equal. The chain drives were connected to the tensile testing rods, between which the specimens were mounted for testing. The resistance wound tube furnace, 13 inches long, could be positioned so that it was directly centered around the specimen. As the machine exerted a tensile load, the equal and opposite motion of the two specimen mounting rods insured that the specimen, as it was being elongated, remained centered in the furnace, thus ensuring that the specimen was maintained at the desired testing temperature. This testing device was found capable of constant strain-rate performance at a load of 500 pounds within a strain-rate range of .03 in/min to 6.0 in/min. The furnace was adjusted so that a temperature of $250^{\circ} \pm 2^{\circ}$ was maintained at the center of the furnace, with less than 1 $^{\circ}$/in thermal gradient along the central 8 inches of the furnace. Beyond this range, but still within the furnace, the thermal gradient was less than 3°/inch.

3. Tensile Tests.

Three tensile specimens were prepared from the alloys, as recorded in Figure 2. Prior to testing they were homogenized at 375°C for 50 hours, quenched in brine, and aged at room temperature for one half hour, during which time the heat evolution took place. A time-temperature record during this phenomenon was maintained for each specimen, and is presented in Section 4.

The specimens were placed in the tensile testing apparatus (illustrated in Figure 3), brought to 265°C, soaked for one hour, and elongated at a constant rate of five inches per minute. After fracture occurred, the fragments were measured and photographed. A portion of each specimen was then mounted and polished for metallographic examination.

Fracture in all three specimens occurred by high temperature intergranular failure. Elongations observed were as tabulated below:

17/83 Al-Zn	75%
20/80 Al-Zn	175%
23/77 Al-Zn	112%

These elongations are not as spectacular as those obtained by Presnyakov (650%) and Backofen (1000%), but they are well beyond normal limits and show a markedly superplastic behavior. The primary purpose in making the tensile tests was to establish the superplastic nature of the alloys used, and to provide the required specimens for subsequent metallographic examination. Quite possibly the two factors primarily responsible for the early intergranular failure were: first, the

surfaces of the specimens were only rough machined; and secondly, the strain rate was higher than that reported by Backofen as yielding the maximum elongation.

Tensile tests were carried out on a number of specimens which were alloyed using the relatively impure Zn (99.9%). Without exception in these cases, the elongations recorded were less than 20%. All procedures outlined for the high purity specimens were followed. This indicates a definite requirement that high purity materials be used if the superplastic effect is to be obtained.

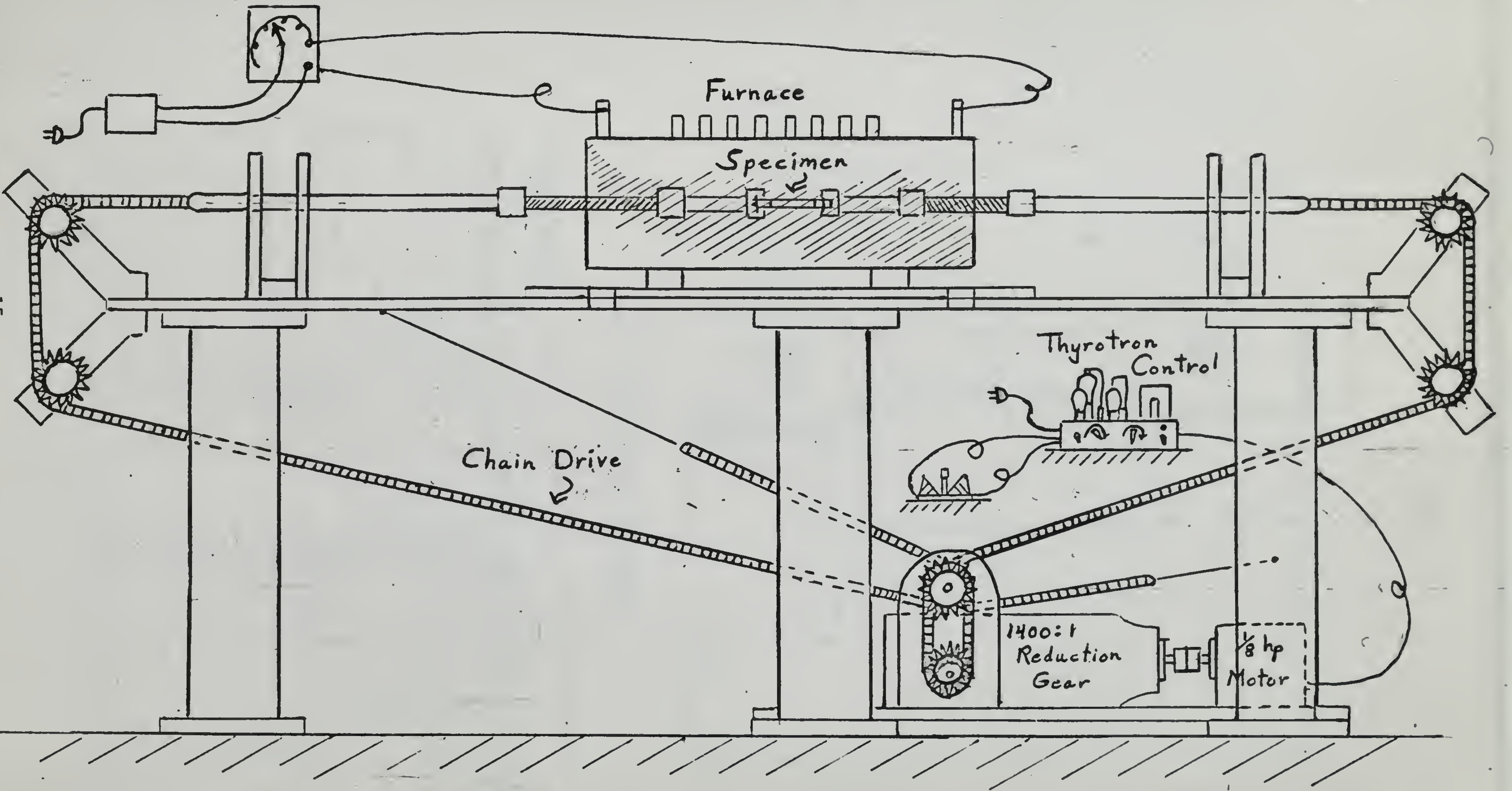

Furnace
Specimen
Thyrotron
Control
Chain Drive
1400:1
Reduction
Gear
1/8 hp
Motor

Figure 2. Sketch of tensile testing apparatus.

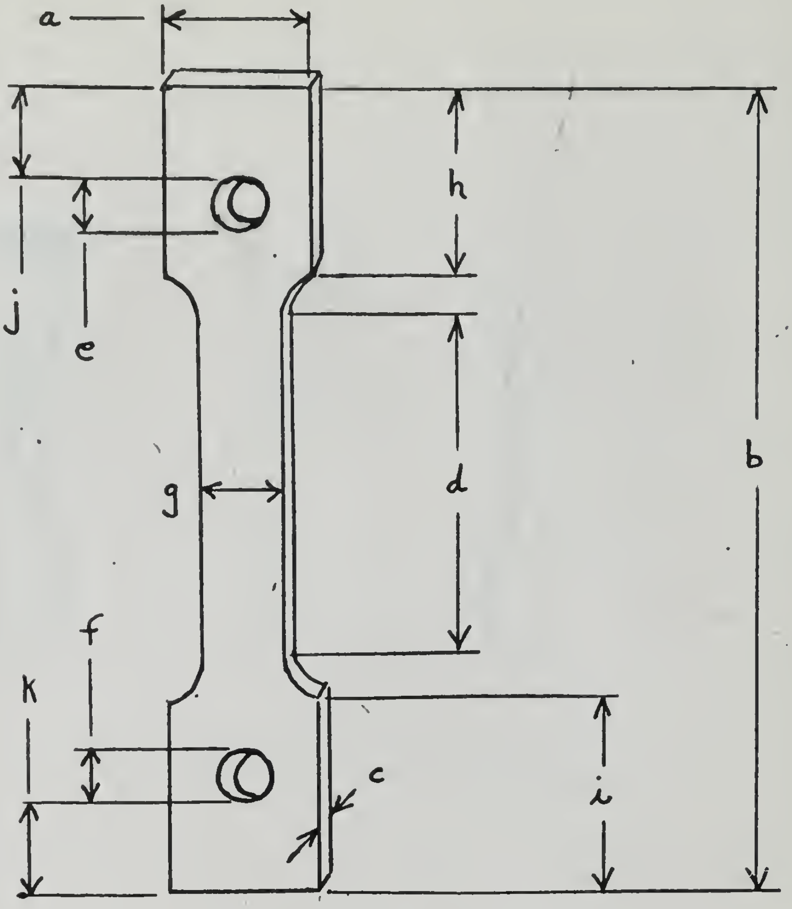


Figure 3. Tensile specimen as machined.

Specimen / Dimension	S 83% Zn-17% Al	M 80% Zn-20% Al	B 77% Zn-23% Al
a	11/16"	3/4"	11/16"
b	3 15/16"	3 15/16"	3 15/16"
c	.089"	.088"	.070"
d	1 5/8"	1 5/8"	1 5/8"
e	3/16"	3/16"	3/16"
f	3/16"	3/16"	3/16"
g	3/8"	3/8"	3/8"
h	7/8"	7/8"	7/8"
i	7/8"	7/8"	7/8"
j	1/4"	1/4"	1/4"
k	1/4"	1/4"	1/4"

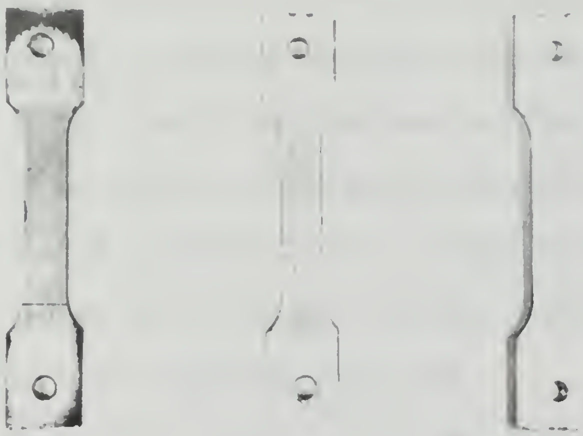


Figure 4. Tensile specimens prior to testing.

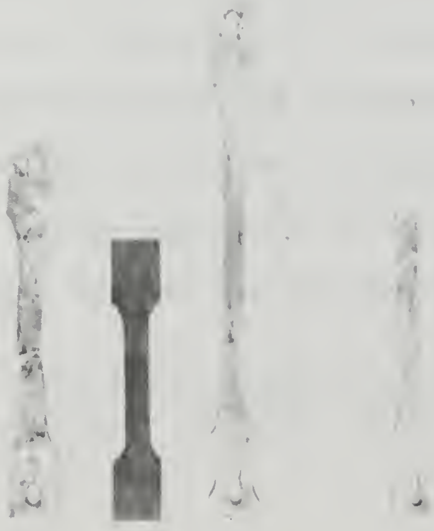


Figure 5. Tensile specimens after elongation. Cutout of original specimen was included for comparison.

4. Heat Evolution

When an Al-Zn alloy which displays a superplastic effect is quenched from above the eutectoid temperature (275°C), a spontaneous evolution of heat occurs. This is believed to be associated with a partial decomposition of the metastable structure resulting from the quench.

After each of the tensile specimens was quenched from 375° to room temperature, a thermocouple was immediately attached to it, and time versus temperature data recorded. This is displayed in Figure 6 in graphical form. During this time the specimens were exposed to ambient air, while resting on an insulating paper mat.

It can be noted that in each of the three alloys the maximum temperature was reached in four to four and a half minutes after quenching.

A second test was performed on a sample of the 20/80 Al-Zn alloy. After soaking at 375° for five hours, the sample was quenched, dried, and immediately immersed in a liquid air bath. This extremely low temperature delayed the decomposition heat release until eight minutes after quenching, but once started, the heat release lasted for twelve minutes. After this period no further activity was noted.

The release of thermal energy at this very low temperature supports the observation made by Ellwood[7] that the phenomenon is not suppressible.

[7] Ellwood, E. C. The Solid Solutions of Zinc in Aluminum. Journal of the Institute of Metals, v. 80, 1951: 217.

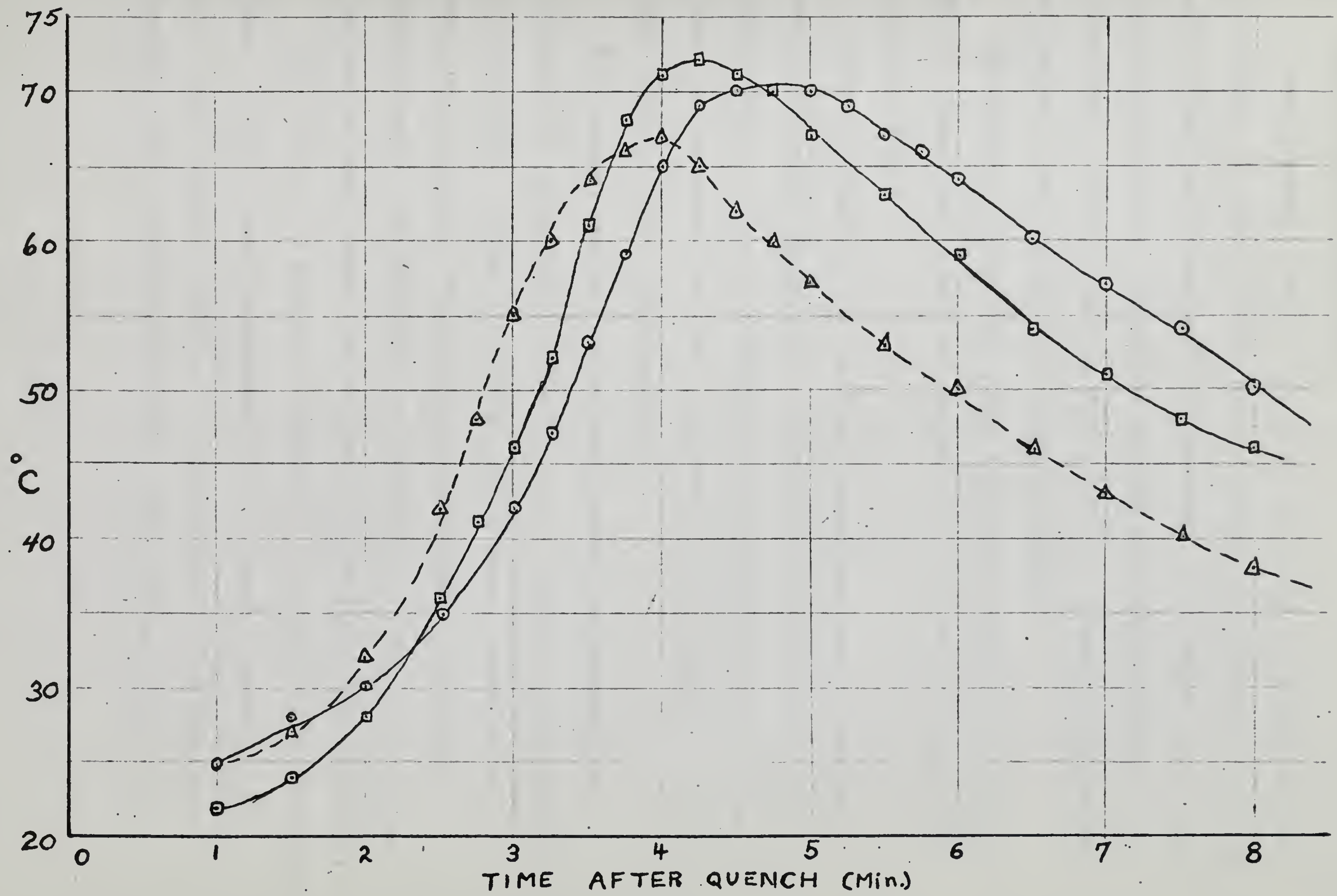


Figure 6. Time temperature plot of heat evolution.

5. Metallographic Observations.

A metallographic study of the three Al-Zn alloys was made in order to determine the characteristic microstructures associated with specific states during the processing of the specimens. As a phase of this study the microstructure was observed as the alloy went through the heat evolution phase following quenching from 375°C in an attempt to determine any changes in the structure that might be visible.

As previously noted, three Al-Zn alloys were studied; 17%, 20%, and 23% Al. Except where noted, all compositions were made with the high purity (99.999%) Zn.

After the specimens were cast and homogenized, samples were cut from each for metallographic use. In the case of the 17% alloy, two samples were cut - one for examination in coordination with the other alloys, and the second for a high temperature quench from the L plus α' region (about 450°C) to room temperature.

This quenched specimen was polished, etched, and examined for characteristic microstructure (See Fig. I-1). Coring is evident within the large grains, showing the α' rich central areas, around which is a nearly eutectic network which shows some precipitate at the grain boundaries and at the interstices of dendrite arms. This is the typical structure one would expect from the phase diagram under these conditions.

Fig. I-2, 3, 4, 5 present a comparison of air cooled 17/83 and 20/80 alloys. In both a nearly homogeneous solid solution is observed, with just a slight pearlitic appearance to the structure. This pearlitic appearance is not resolved at the higher magnifications of Fig. I-4, 5,

but is in evidence in the lower magnifications. This appearance could be attributed to a clustering of vacancies (porosity) or a clustering of precipitate particles.

An extension of this study was made by soaking the 20/80 air cooled sample at 270°C (just five degrees below the eutectoid temperature) for four hours. This treatment fully developed a typical pearlitic structure. A few rosettes are in evidence, and are indicative of localized eutectoid melting. See Fig. I-6.

Fig. I-7 to Fig. I-15 show the typical microstructures developed by quenching from 375° to room temperature. This quench is followed by a period of rather intense heat evolution which lasts for about ten minutes. (This phenomenon was discussed in more detail in Section 4.)

An attempt was made to obtain a micrographic record of the structure as this heating occurs to determine what, if any changes were evident in the surface structure of the specimen.

To conduct this study the specimens were carefully polished and etched, and heated for ten hours at 375°C. Immediately after quenching, the specimens were touched up briefly using a 3 micron wheel, followed by a 1 micron wheel, reetched, and immediately photographed. The time required for these steps was about three minutes.

The specimens were then aged for one day at room temperature, thoroughly polished to remove any traces of surface film, etched, and reexamined.

In no case was any structural change observed during or immediately after the heat evolution phase. This conclusion was reinforced by subsequent observations at high magnification of these and other samples,

including some which contained the lower purity Zn (99.9%). This can be noted by a comparison of Fig. I-7, parts a. and b., and of Fig. I-13, a. and b.

In conducting this series of observations, it became obvious that care had to be taken during the rapid polishing following the quench in order to insure adequate removal of the surface oxide layer. Failure in this regard can lead to completely misleading data, as illustrated in Fig. I-10 and Fig. I-11.

One observation of some interest results from a comparison of the micrographs taken immediately after quenching and those of the corresponding structures taken after aging for one day. Fig. I-9d shows a clearly defined finely precipitated phase which is not evident in Fig. I-8b. This same type of effect is also noted in a comparison between Fig. I-14 and Fig. I-15. The latter figure shows a fine precipitated structure which clusters around the grain boundaries, while the former only indicates a formless, uniformly distributed darkening of the matrix material.

This change is apparently due to a surface migration effect in conjunction with the aging of the alloy. That aging does take place is documented in the X-ray diffraction section of this report. Clustering effects in Al-Zn alloys were investigated by Rudman, Flinn, and Averbach,[8] and also by Turnbull, Rosenbaum and Treaftis.[9] Their results

[8] Rudman, P. S., Flinn, P. A., and B. L. Averbach. Measurements of Clustering in Solid Al-Zn Alloys. Journal of Applied Physics, v. 24, 1953: 365.

[9] Turnbull, D., Rosenbaum, H. S., and H. N. Treaftis. Kinetics of Clustering in Some Aluminum Alloys. Acta Met., v. 8, 1960: 278.

indicated that solute rich (i.e., Zn rich) clusters, which are coherent with the parent solid solution form at comparitively low temperatures.

Each of the stages is illustrated in the figures by micrographs of different magnifications, in order to give as clear an indication as possible of the overall appearance and structure as well as the fine detail. In attempting magnification beyond the resolving power of the metallograph used, Fig. I-12b became somewhat indistinct, but is nonetheless included since it reveals aspects of the structure which are not clearly illustrated by the other magnifications of the same view.

After the specimens were tested in the tensile apparatus, a sample of each was taken from a region adjacent to the fracture area which corresponded to the area of greatest strain in the specimen. After polishing and etching, each specimen was examined and photographed. These micrographs are presented in Fig. I-16 to Fig. I-18.

Fig. I-16 corresponds to the 17/83 Al-Zn alloy, and shows a fine precipitate structure which contains some apparently platelike, evenly dispersed quantities of proeutectoid β phase, in about the amount that would be expected for a hypoeutectoid alloy of this composition.

Fig. I-17 shows the structure of the 20/80 alloy, which gave by far the greatest elongation in the tensile tests. It is an uninterrupted, uniformly fine precipitate dispersed in a lighter matrix material. This structure was found without exception to extend over the entire surface of the specimen. The appearance is what one would associate with the eutectoid composition, despite the fact that the actual composition is 2% removed from the eutectoid.

The third alloy is illustrated in Fig. I-18, and shows the same type of structure as did the 17/83 alloy, except that the included proeutectoid phase does not have the semi-regular platelike appearance, but is globular in nature. In this case the proeutectoid is α phase, as is to be expected in an Al rich alloy.

Conclusions based on this metallographic study as regard any observable structural change during heat evolution are negative; that is, no changes were observed. However, the clustering effect, as noted in the discussion, is of some interest as it points to kinetic activity of considerable magnitude in the alloy when quenched into a metastable state. The microstructures observed are largely those to be expected from the alloy compositions involved, and as such introduce no new considerations into the study of the alloy system.

6. Diffraction Analysis.

Presnyakov studied the relationship between degree of superplasticity and departure from equilibrium lattice parameters in an earlier study of 20/80 Al-Zn alloys, and found lattice parameters varying from 4.0384 Angstroms for the slowly cooled alloy (equilibrium) to 4.0414 Angstroms for the quenched alloy (metastable). The greatest superplastic effect was in the alloy with the greatest departure from the equilibrium lattice spacing [3].

To help in interpretation of the microstructures observed at the different stages of heat treatment and aging, it was intended to use X-ray analysis to determine the phases and compositions present. It became evident that the only phases present were the solutions of zinc and aluminum so it seemed that X-ray analysis would serve only to follow changes in lattice parameters.

The X-ray measurements were made with a Norelco Diffraction Unit and Copper K radiation filtered with Nickle to minimize the Beta radiation with respect to the Alpha radiation. Peaks at approximately 2θ equal to 138.95 degrees associated with the (212) plane in the hexagonal close-packed structure of zinc and 2θ equal to 137.46 degrees associated with the (422) plane in the face-centered cubic structure of aluminum were followed.

These peaks were chosen because they provide a reasonable balance between intensity and precision of lattice parameter measurements when scanned at the rate of 1/8 degree per minute. However, the 32 minutes required to scan these peaks precluded studying the lattice changes occurring during the heat evolution previously noted. Because the

initial peaks were so broad and the shape of the peaks changed gradually as a slow structural change occurred, attempts to measure meaningful "lattice parameters" in an undefined structure were abandoned.

The diffraction peaks attained are displayed in Appendix II. Figures II-1 to II-5 pertain to the 17/83 alloy. Scans for this alloy were made beginning immediately after quench, quench plus 24 hours, quench plus 31 hours, quench plus 74 hours and quench plus 104 hours. Figures II-2 to II-10 pertain to the 20/80 alloy. Scans for this alloy were made beginning immediately after quench, quench plus 24 hours, quench plus 31 hours, quench plus 48 hours, and quench plus 80 hours. Figures II-11 to II-19 are patterns from the 23/77 alloy which were made immediately after quench, quench plus 1 hour, 2 hours, 3 hours, 11 hours, 23 hours, 37 hours, 49 hours, and finally, 100 hours.

As can be readily seen by examination of the scans, the diffraction traces for all three alloys immediately after quenching exhibit very poor resolution of peaks. Subsequent traces are increasingly better resolved but accurate measurement of lattice parameters could not be made until after 75 hours following quench. At this time, transformation from the α' phase to the two phase region of α and β phases is complete, or nearly so. The transformation which occurs under equilibrium conditions at 275 degrees Centigrade cannot be suppressed by quenching for Al-Zn alloys containing more than 33 atomic per cent zinc [4].

Following the initial studies, diffractometer runs were made over the complete scan from values of 2θ equal to 35 degrees to 2θ equal to 148 degrees for each of the three specimens. These runs

were made at a rate of 1/2 degree per minute. At this speed resolution of peaks was good but exact measurements were not possible. However, all three specimens exhibit similar peaks at approximately the same value of 2θ for each significant line. These peaks can be readily identified as those associated with the terminal solutions of zinc and aluminum. Table 1. tabulates these results for the 23/77 alloy and compares them with peaks for zinc and aluminum. The symbol "d" indicates the interplaner spacing associated with the planes designated by their respective values of hkl.

The unresolved peaks in the diffraction patterns taken immediately after quench require further consideration. These interesting, anomalous results present strong evidence of a decided departure from a three-dimensional periodicity of structure. Normal, three-dimensional, crystals give diffraction patterns which display well-resolved sharp peaks. If a precipitate is forming during aging of such "normal" alloys or materials, the original peaks become broader when compared in a series of diffractometer patterns analogous to the series taken in this investigation. Three-dimensional crystals do give peaks which are also broadened by small particle size or strain. If the strain is large enough or is systematic, periodicity can be lost in one or more directions. One and two-dimensional structures have been studied in other systems and there is some information available on the patterns to be expected for specific conditions. Small enough particle size also means disappearance of periodic repetition in space.

The fact that in the series of patterns taken for this investigation, broad undefined peaks which gradually change into well-defined

	Aluminum			Zinc			23/77 Al-Zn	
Line	d	I/I_1	hkl	d	I/I_1	hkl	d	I/I_1
1				2.473	53	002	2.4728	50
2	2.338	100	111				2.3364	40
				2.308	40	100	2.3133	40
4				2.091	100	101	2.0925	100
5	2.024	47	200				2.0257	20
6				1.687	28	102	1.6881	30
7	1.431	22	220				1.4317	10
8				1.342	25	103	1.3430	25
9				1.332	21	110	1.3330	25
10				1.237	2	004	1.2374	2
11	1.221	24	311				1.2214	10
12				1.1729	23	112	1.1730	25
13	1.1690	7	222				1.1694	1
14				1.1538	5	200	1.1534	5
15				1.1236	17	201	1.1242	20
16				1.0901	3	104	1.0903	3
17				1.0456	5	202	1.0456	5
18	1.0124	2	400				1.0130	1
19				0.9454	8	203	0.9462	10
20	0.9289	8	331				0.9291	3
21				0.9093	6	105	0.9093	5
22				0.9064	11	114	0.9063	10
23	0.9055	8	420				0.9054	3
24				0.8722	5	210	0.8724	5
25				0.8584	9	211	0.8589	10
26				0.8437	2	204	0.8439	2
27	0.8266	8	422				0.8265	3
28				0.8245	1	006	0.8246	1
29				0.8225	9	212	0.8226	10

Table 1. Compilation of Tabulated Values of "d" for Zinc and Aluminum compared with observed values of "d" for experimental 23/77Al-Zn Alloy.

[illegible]

[illegible]

peaks indicative of the terminal constituents of zinc and aluminum solid solutions occur, indicates that initially a disordered structure lacking complete three-dimensional periodicity is present. Considering Presnyakov's postulate that in the breakdown of the metastable stage into the equilibrium phases, superplasticity arises during the latter stage of the breakdown, the slow process observed in this diffraction analysis suggests the mechanisms involved and a direction for further investigation. If, as Presnyakov postulates, this second or latter stage of breakdown is connected with a weakening of the interatomic bond during the reconstruction of the crystallin lattice 3 , the interpretation that the reconstruction of the lattice is, in fact, the construction of a three-dimensional lattice logically follows.

It would be of interest to compare the diffractometer patterns obtained in this investigation with the results of diffraction analysis taken on the same samples after they had been soaked at 265 degrees Centigrade for one hour, as were the tensile specimens, and then quenched. It would alos be of interest to compare the speed with which this transformation takes place when compared with diffraction traces obtained at lower temperatures, i.e. room temperature, during this investigation as displayed in Appendix II.

7. Discussion of Results.

The broad, undefined peaks shown by the diffractometer tracings taken immediately after quenching indicate the type of disordered state found in glass-like materials. This disorganized structure could result from vacancy generation by the elimination of stacking faults in the highly faulted structure of the α' solution.

Because of the limits of optical resolution in the photomicrographs, it is not possible to dismiss completely the possibility than an extremely small particle size in the metastable state (immediately following quench) is the reason for the disappearance of periodic repetition in space, as displayed in the initially broad peaks on the diffractometer tracings.

As the aging time of the specimens increased, the peaks on the diffractometer traces associated with the equilibrium phases became well defined and strong, indicating that an ordering and/or precipitation effect is active at room temperature. Further evidence of this is available in the metallographic study, where the clustering effect after aging was pointed out. In the micrographs it is not possible to determine whether the clustered regions result from a migration of vacancies or precipitate particles, but in either case a definite diffusion process is indicated. Vacancy clustering could result in a highly porous region at the grain boundaries, while precipitate migration could result in a darkened area of clustered precipitate, both giving the same surface appearance.

Due to the delay time involved in diffractometer analysis, comparative observations before and after heat evolution cannot be used to supplement metallographic observations during the heat evolution. However,

metallographic examination shows that no observable change takes place during the intense heat liberation. The most likely explanation of this phenomenon lies in the breakdown of the unstable α' phase to the metastable - but undefined - structure remaining after the heat evolution. Here the early, broad peaks indicate a disorganized, metastable structure. The developing peaks, in conjunction with the metallographic evidence of clustering indicate diffusional mechanisms are at work to relieve the stresses and to generate a more organized and regular structure.

Among the various observations in this investigation, primary interest centers upon the initial, and unexpected, disordered state of the quenched alloys as evidenced in the diffractometer traces. If, upon further investigation, the phase transformation taking place at such a relatively slow rate at room temperature can be correlated with the analogous transformation or reordering, as postulated by Presnyakov, perhaps the causes or mechanisms involved in the phenomenon of superplasticity can be understood.

8. Acknowledgements.

Our appreciation and thanks are extended to Mr. Roy F. Edwards and Mr. William D. Penpraze for their generous and capable assistance as laboratory technicians, and to Professor G. D. Marshall, who gave willingly of his time and knowledge during the course of this investigation.

To Professor John R. Clark, our patient and unselfish thesis advisor, goes our sincere gratitude for his continuous assistance and direction.

BIBLIOGRAPHY

1. De Jong, M. Mechanical Properties of Iron and Some Iron Alloys During Allotropic Transformation. Thesis, University of Amsterdam, 1960.

2. De Jong, M. and G. W. Rathenau. Mechanical Properties of Iron and Some Iron Alloys While Undergoing Phase Transformation. Acta Met., v. 7, 1959: 246.

3. Underwood, E. E. A Review of Superplasticity and Related Phenomena. Journal of Metals, v. 14, 1962: 914.

4. Ellwood, E. C. The Solid Solutions of Zinc in Aluminum. Journal of the Institute of Metals, v. 80, 1951: 217.

5. Backofen, W. A., Turner, I. R., and D. H. Avery. Superplasticity In An Al-Zn Alloy. Advance copy prior to publication, MIT, June 29, 1964.

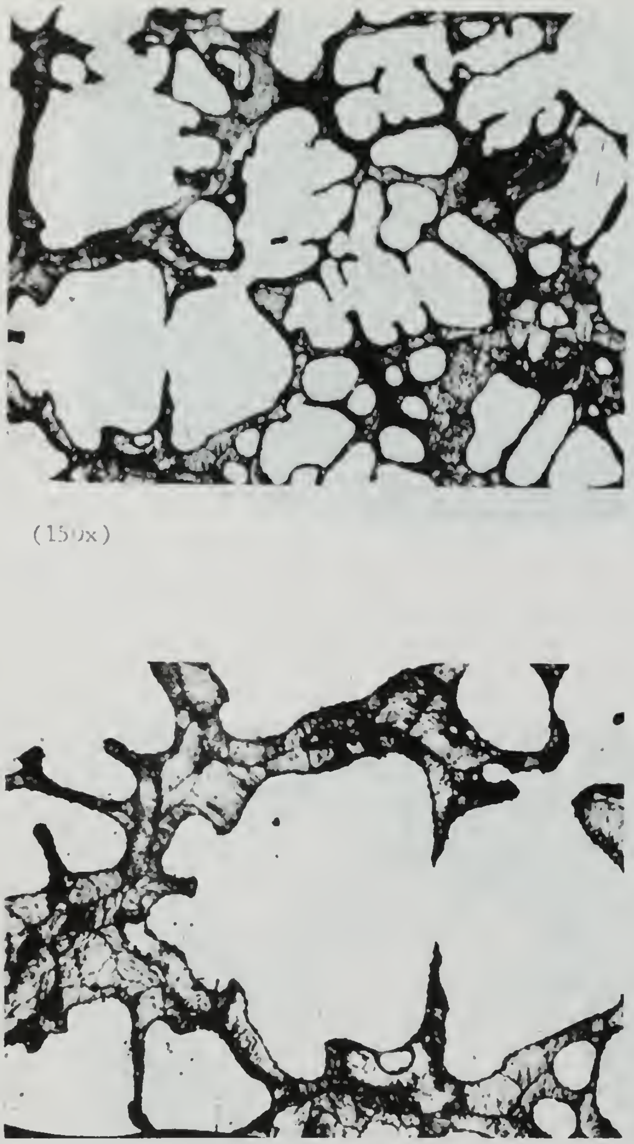
6. De Jong, M. and G. W. Rathenau, Mechanical Properties of an Iron-Carbon Alloy During Allotropic Transformation. Acta Met., v. 9, 1961: 714.

7. Cottrell, A. H. Dislocations and Plastic Flow in Crystals. The Clarendon Press, Oxford, England, 1953: 182-185.

8. Read, W. T. Jr. Dislocations in Crystals. McGraw-Hill Co., New York, 1953: 49-79.

APPENDIX I

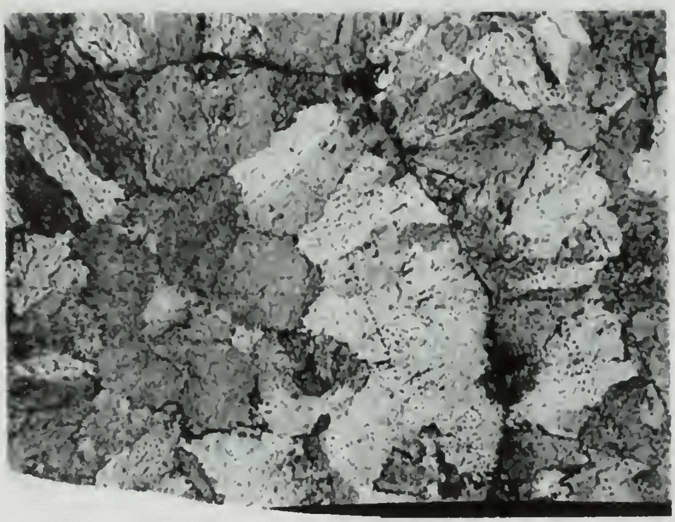
PHOTOMICROGRAPHS



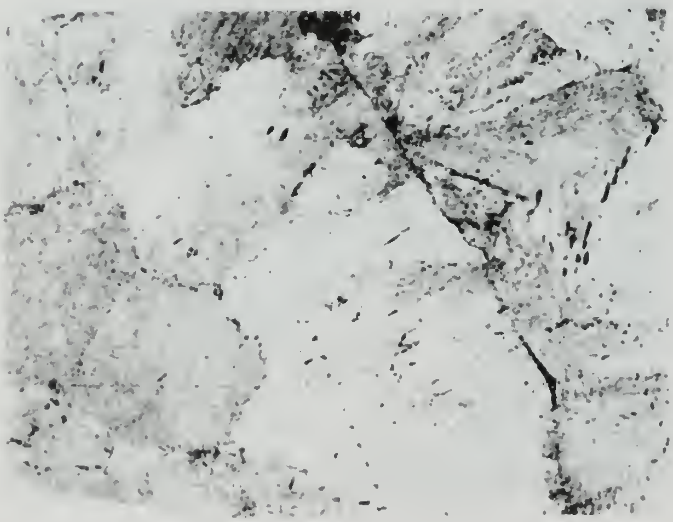
a. (150x)

b. (300x)

Fig. I-1. 17/83 Al-Zn alloy, air cooled from liquidus to L plus α' region at 450°C, then quenched in brine to room temperature.

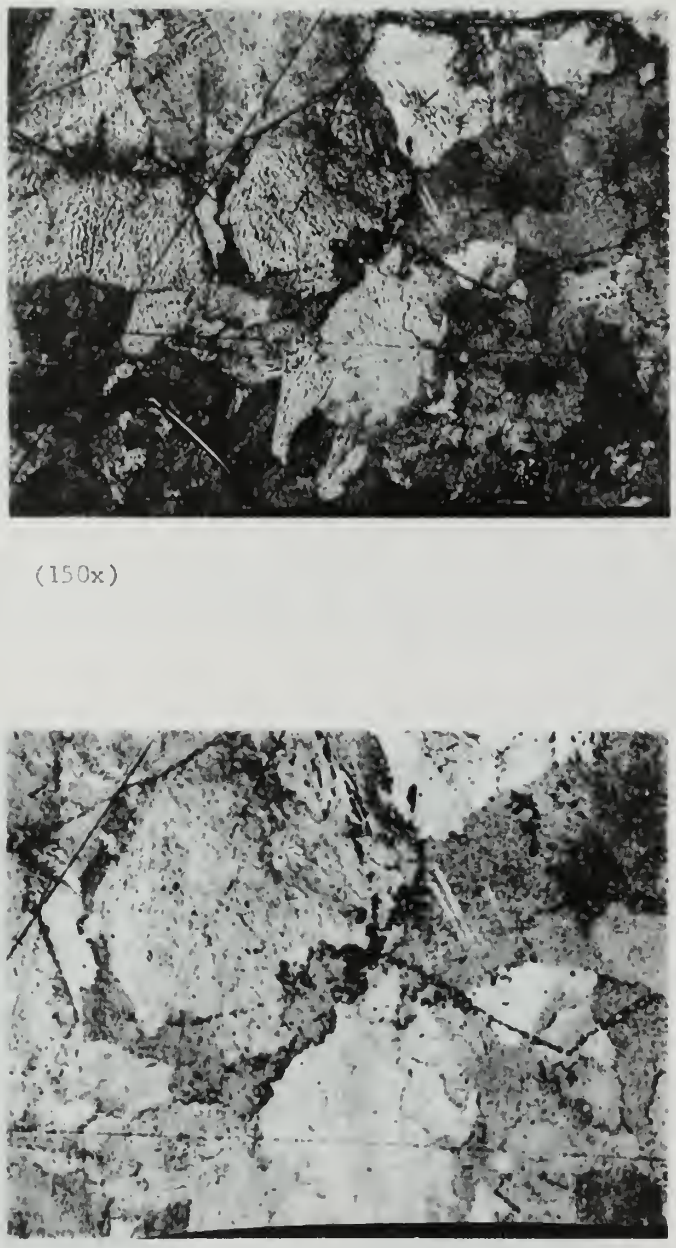


a. [illegible]



b. (300x)

Fig. I-2. 17/31 Al-Zn alloy, air cooled from α' plus β two-phase region (375°C).



a. (150x)

b. [illegible]

Fig. I-1. 70/30 Al-Zn alloy, air cooled from α' plus β two phase region (375°C).

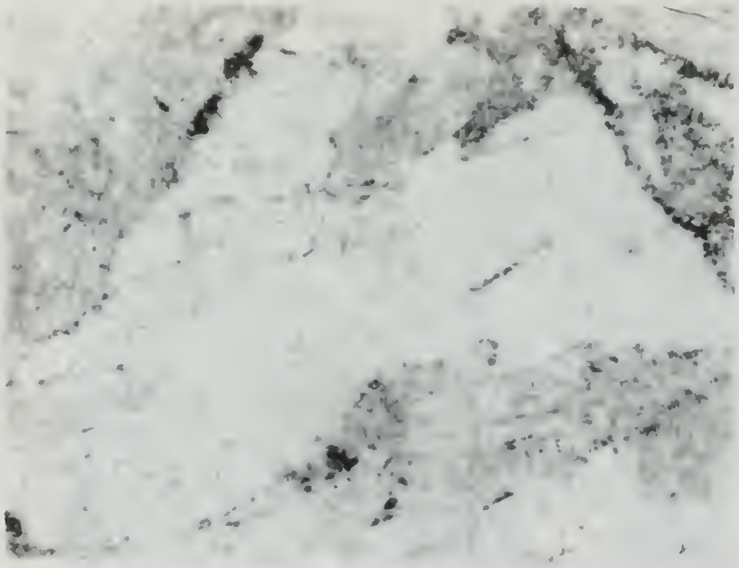


Fig. I-4 17/83 Al-Zn alloy (800x). Air cooled from α′ plus β two phase region (375°C).

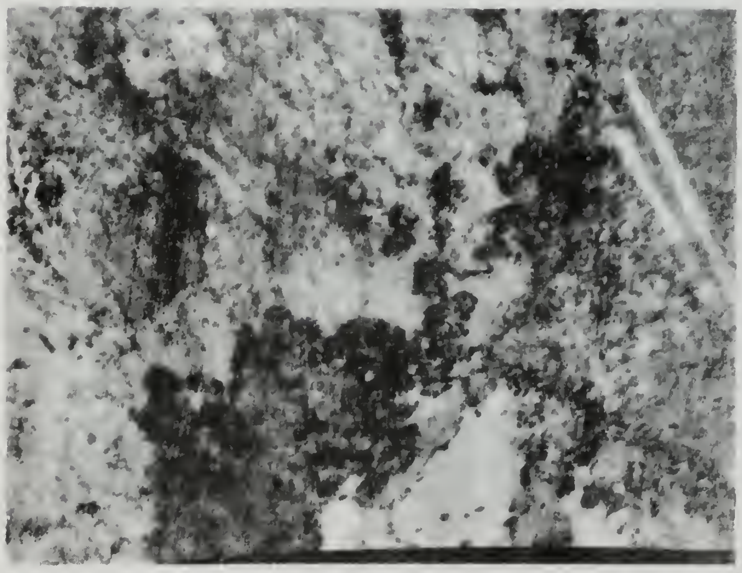
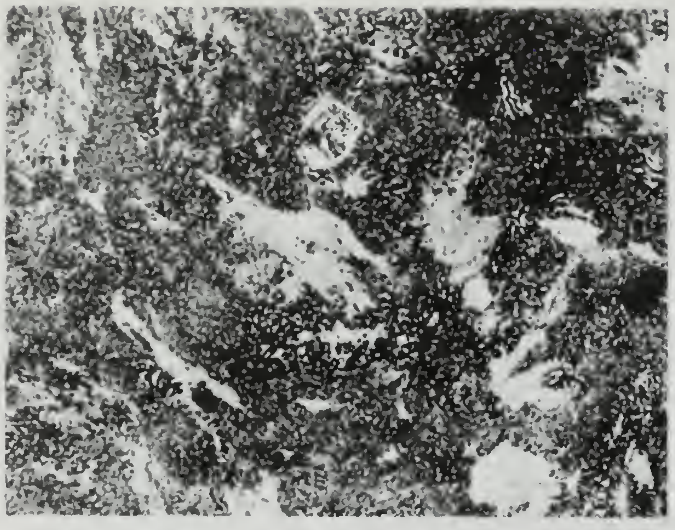
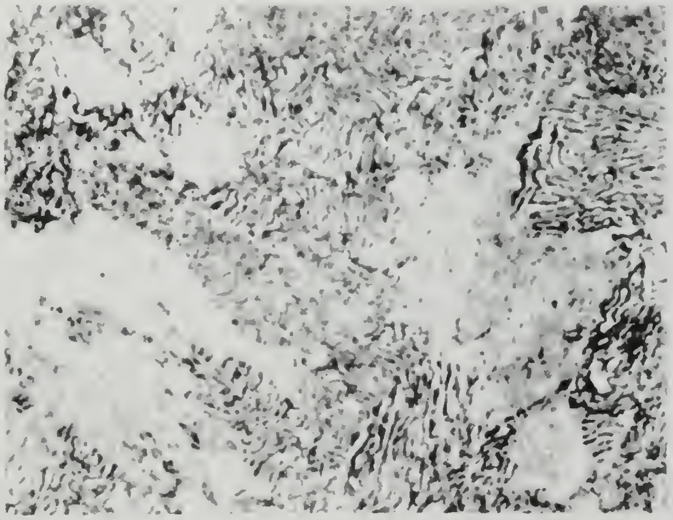


Fig. I-5. 20/80 Al-Zn alloy (800x). Air cooled from α′ plus β two phase region (375°C).





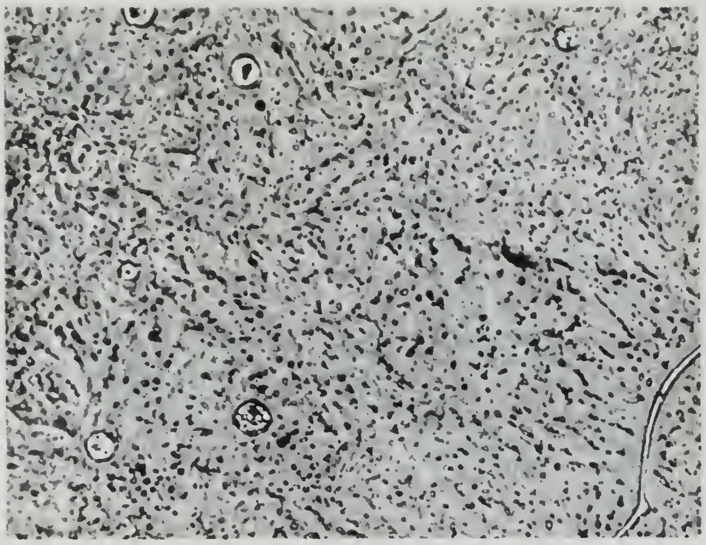
b. [illegible]

[illegible] cooled from [illegible] to room temperature, then [illegible] at [illegible]°.

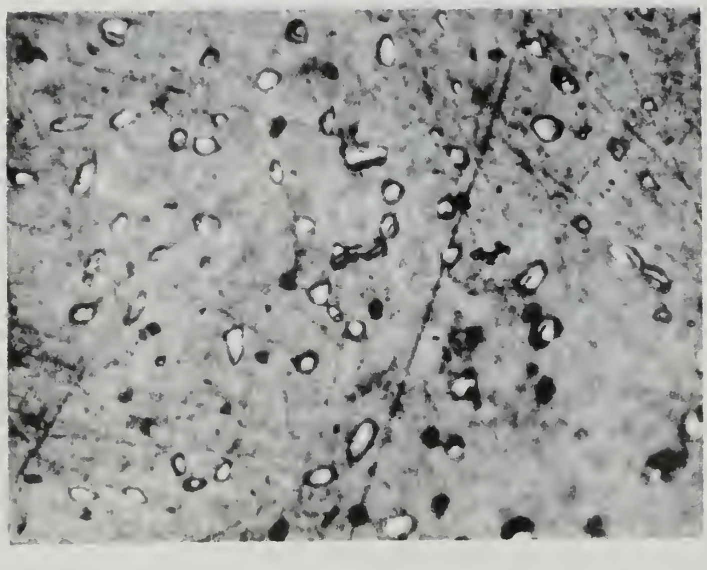
a. (300x) Four minutes after quenching from 375°.
During heat evolution

b. (300x) Eleven minutes after quenching from 375°.
Same area as above, but after heat evolution.

Fig. I-7. 17/83 Al-Zn alloy.

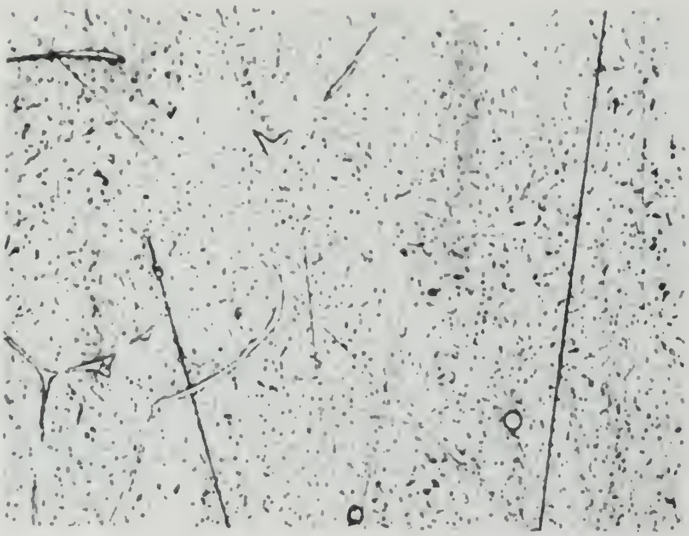


a. (150x)

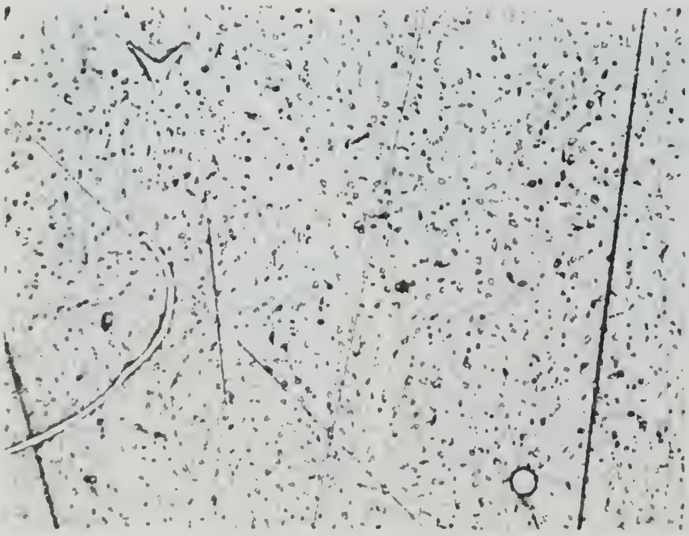


b. (800x)

Fig. I-8. 17/83 Al-Zn alloy, quenched in brine from 375°C. Slight polish and etch after quenching.

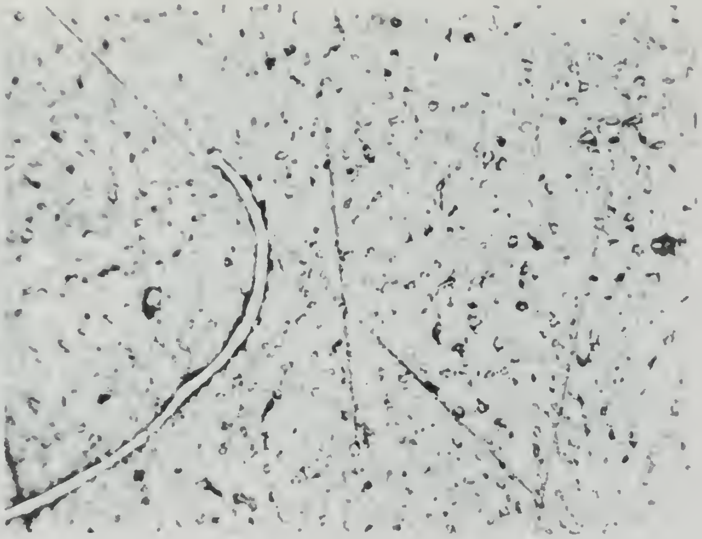


a. (80x)

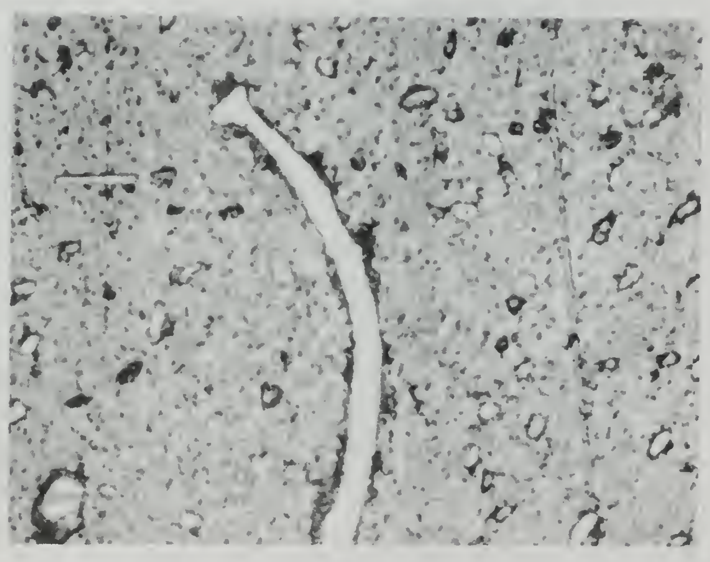


b. (150x)

Fig. I-9. 17/83 Al-Zn alloy. Same specimen as Fig. I-7, 8, except surface film removed by heavy polishing followed by reetching. Aging time prior to repolishing was 1 day.



a. (300x)



b. (800x)

Fig. I-9 (continued). 17/83 Al-Zn alloy. Same specimen as Fig. I-7, 8, except surface film removed by heavy polishing followed by reetching. Aging time prior to repolishing was 1 day.

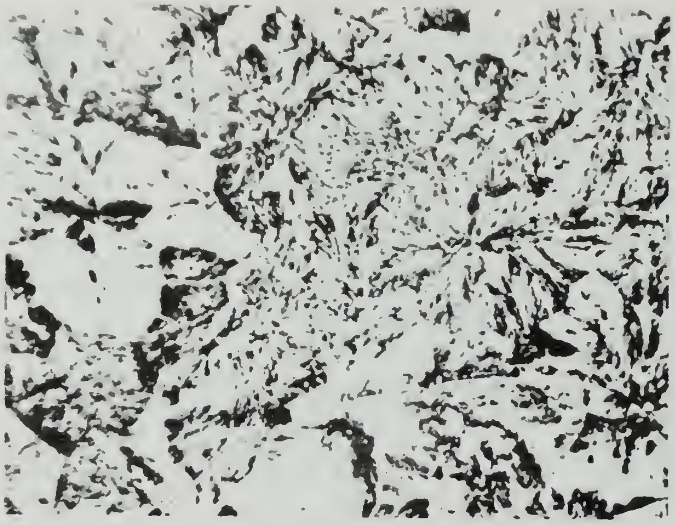


Fig. I-10. 20/80 Al-Zn alloy (300x). Specimen held at 375°C for 10 hours, quenched in brine, lightly polished, and etched.

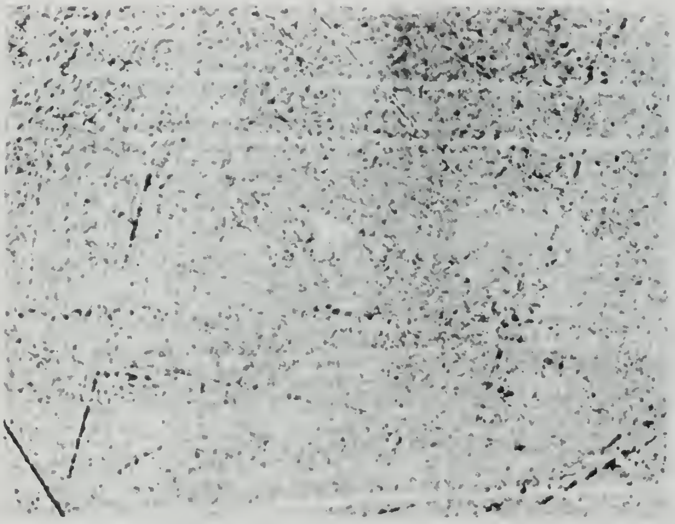
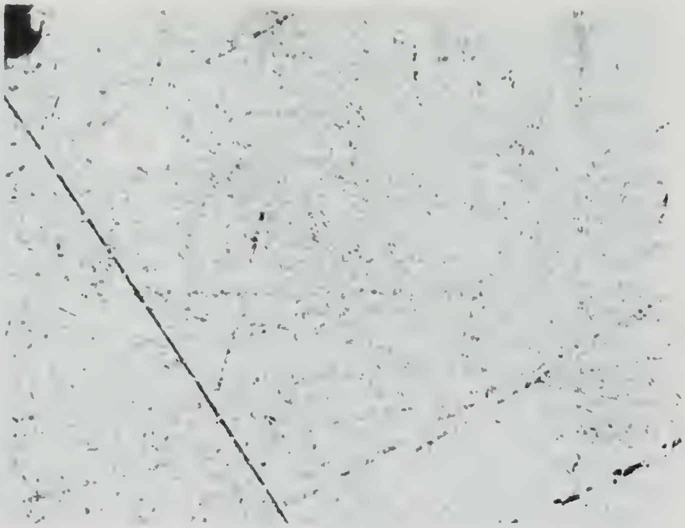
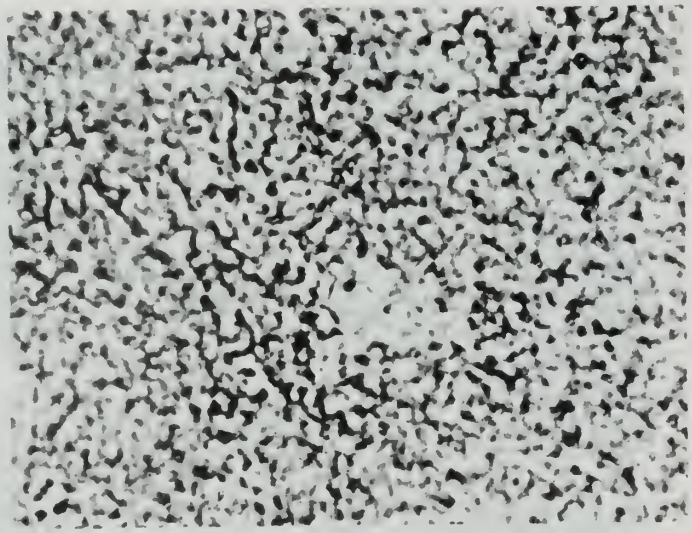


Fig. I-11. (300x). Same specimen as above, but after thorough polishing to remove all surface film. Reetched. Note complete change of appearance.

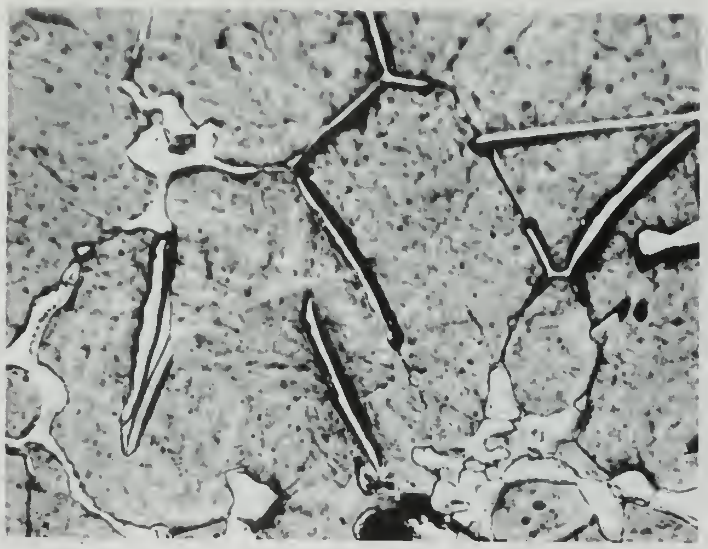


[illegible]

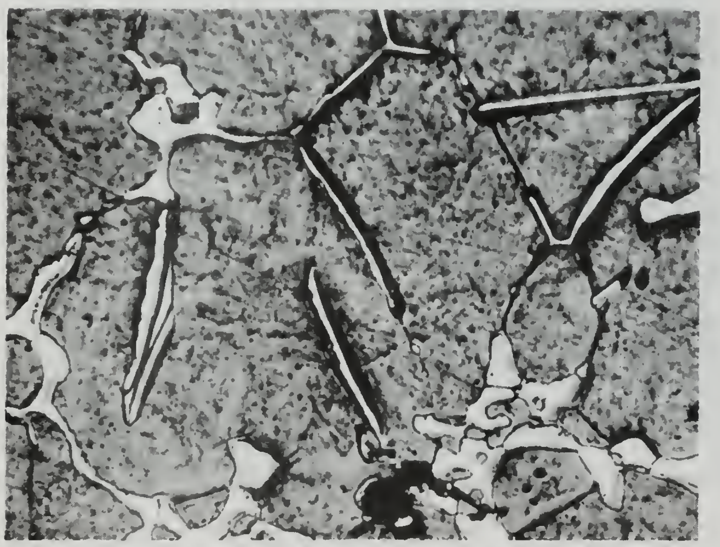


[illegible]

Fig. I-17. Same specimen as in Fig. I-11. Large and small scale [illegible].

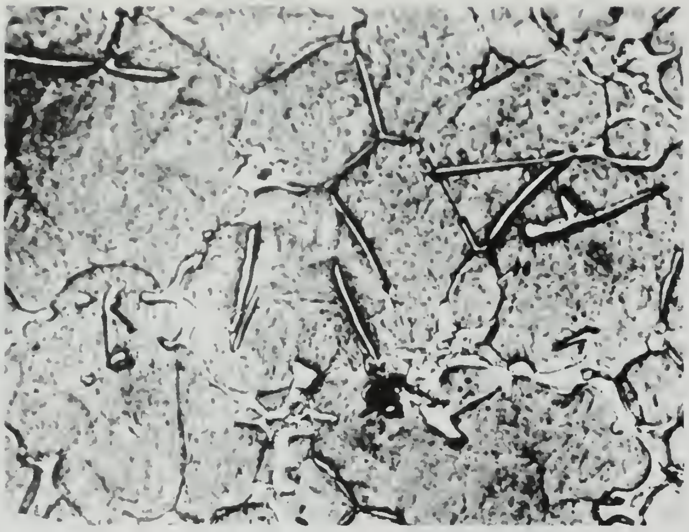


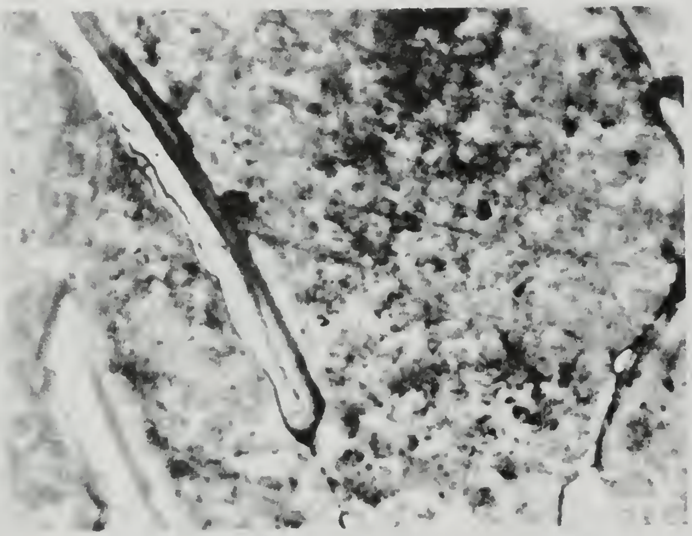
a. (300x) Two minutes after quench; before heat evolution.



b. (300x) 55 minutes after quench; after heat evolution.

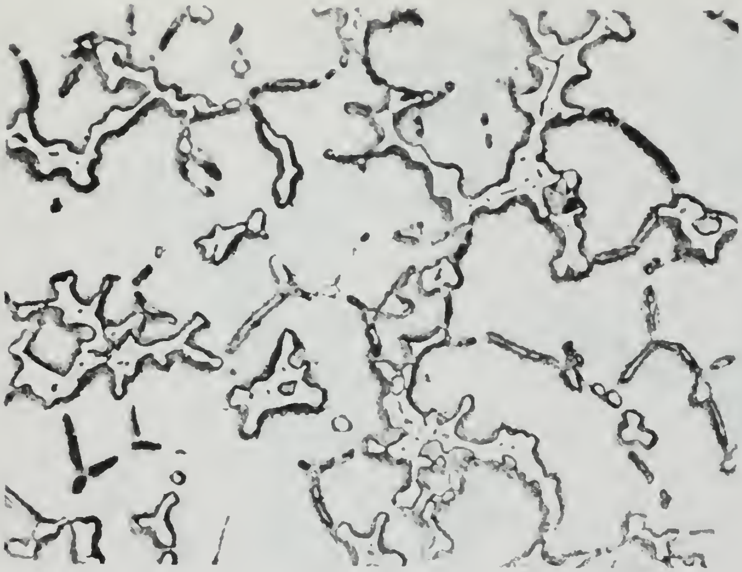
Fig. I-13. 23/77 Al-Zn alloy. Polished, etched, and soaked at 375°C for 10 hours. Quenched to room temperature, polished lightly, and etched. Note no discernable change before and after heat evolution.



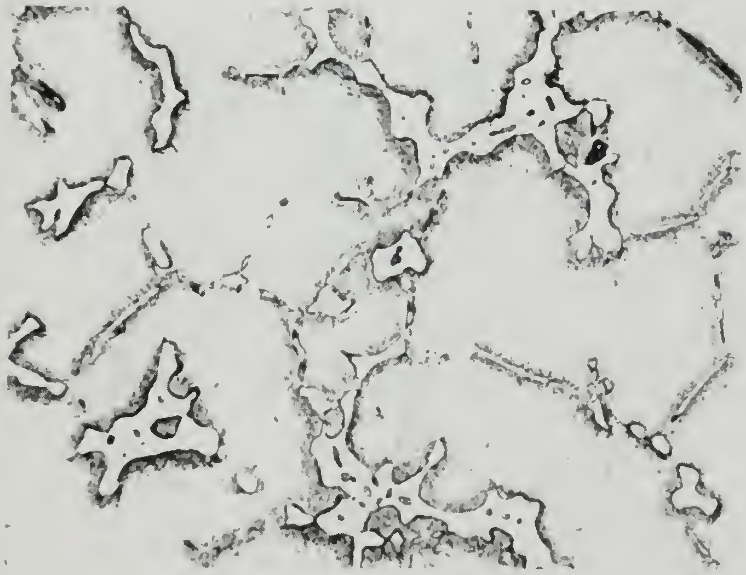


([illegible]x)

Fig. I-14. Same specimen as Fig. I-13. One hour after [illegible].

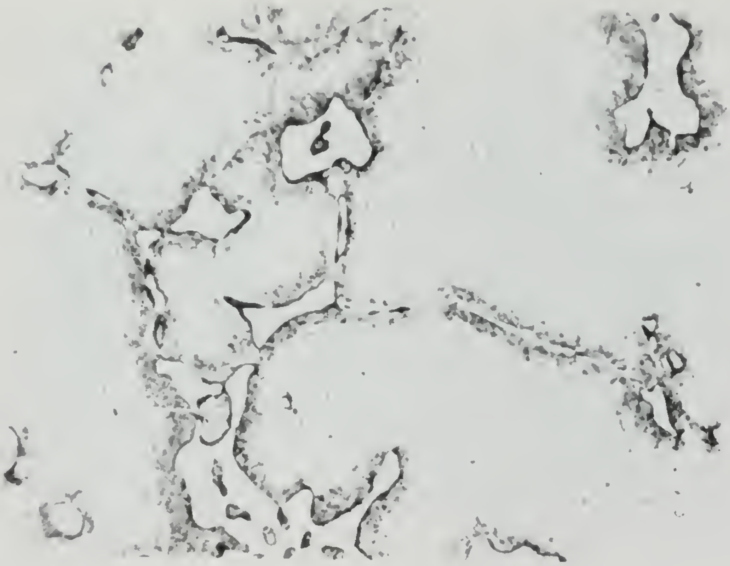


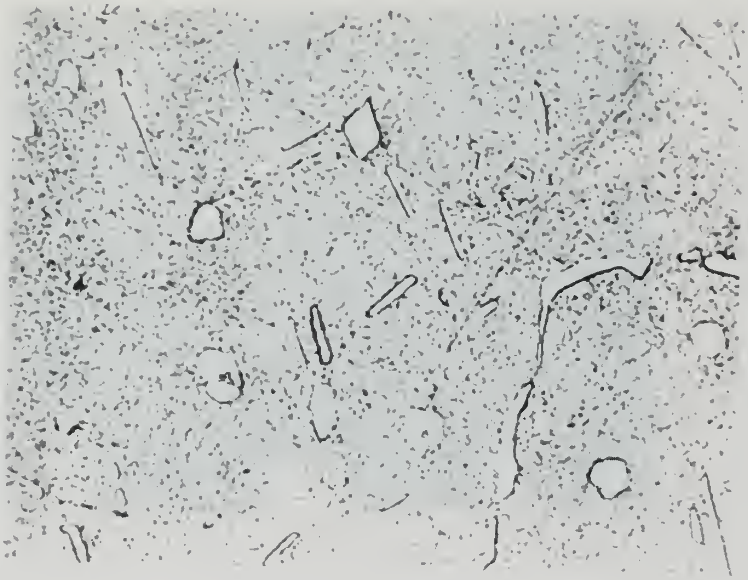
a. ([illegible])

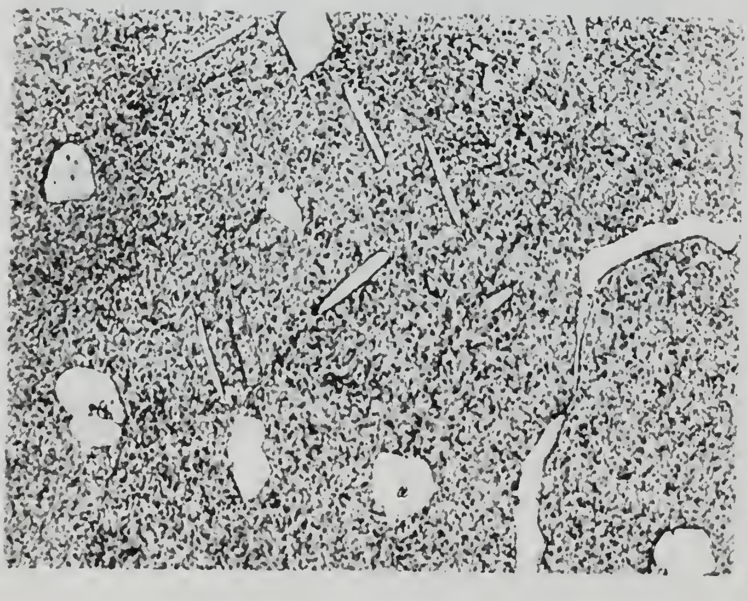


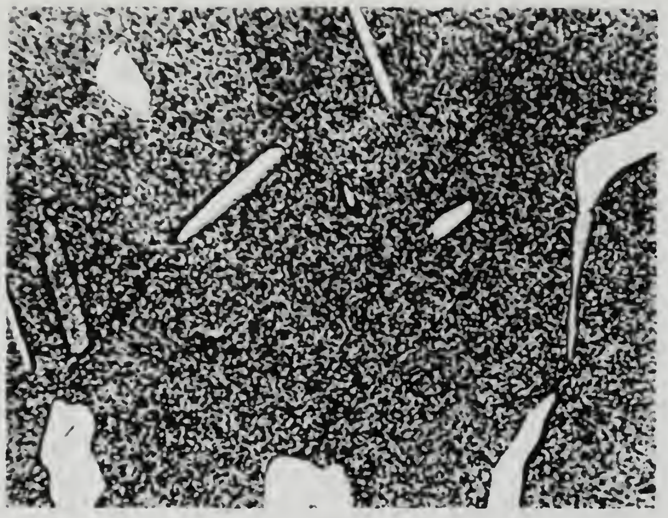
b. (150x)

Fig. I-15. 23/77 Al-Zn alloy. Same specimean as Fig. I-13, 14, except thoroughly repolished and etched to remove all trace of surface film. Note fine precipitate not evident in Fig. I-13, 14.

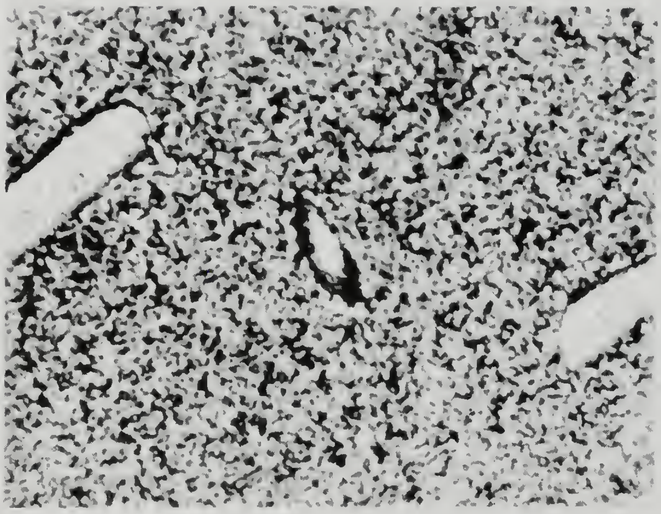






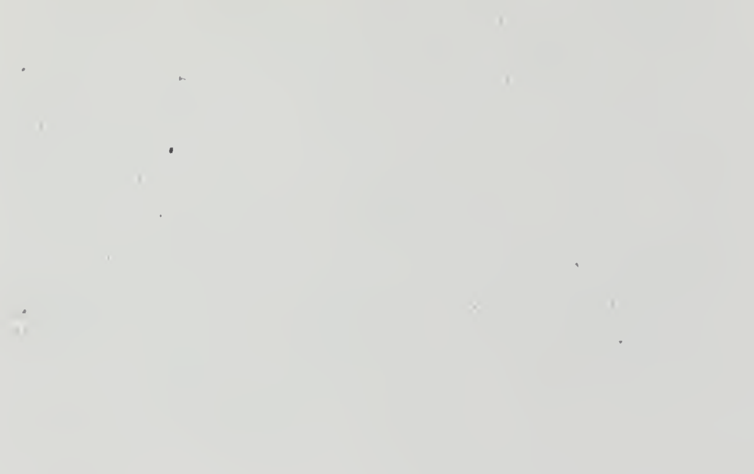


c. (300x)



d. (800x)

Fig. I-16 (continued). 17/83 Al-Zn alloy. Micrograph of tensile specimen near point where fracture occurred.



[illegible]

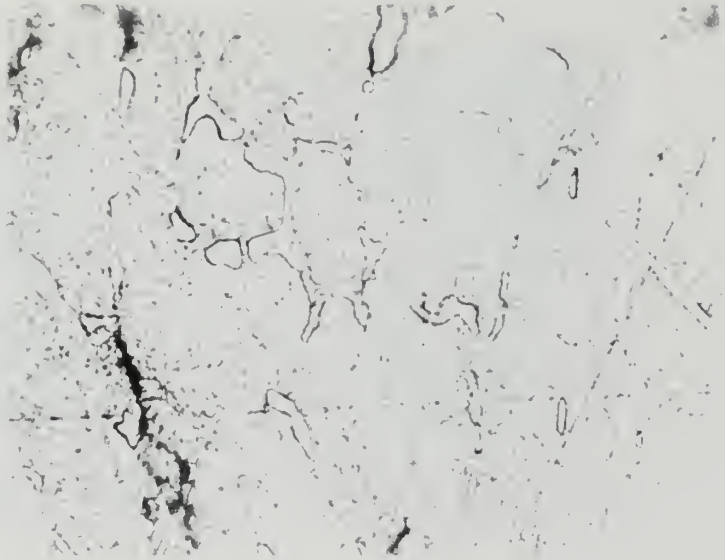
(150x)

[illegible] I-17. 20[illegible] Al-Zn alloy. Micrograph [illegible] tensile [illegible] near point where fracture occurred.

c. (200x)

d. (800x)

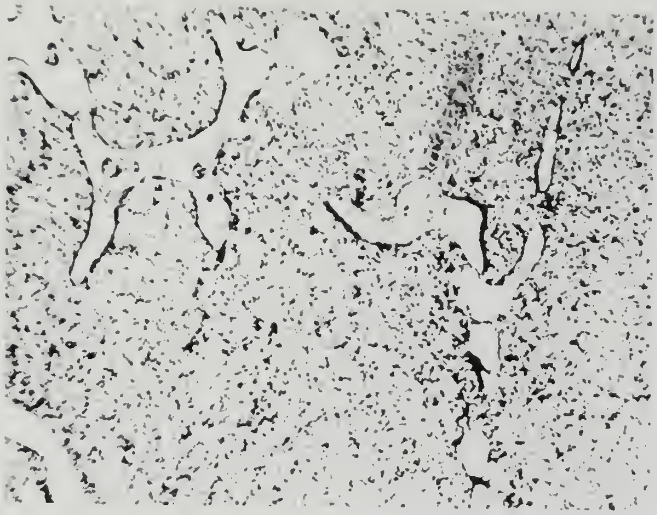
Fig. I-11 (continued). 20/80 Al-Zn alloy. Micrograph of tensile specimen near point where fracture occurred.



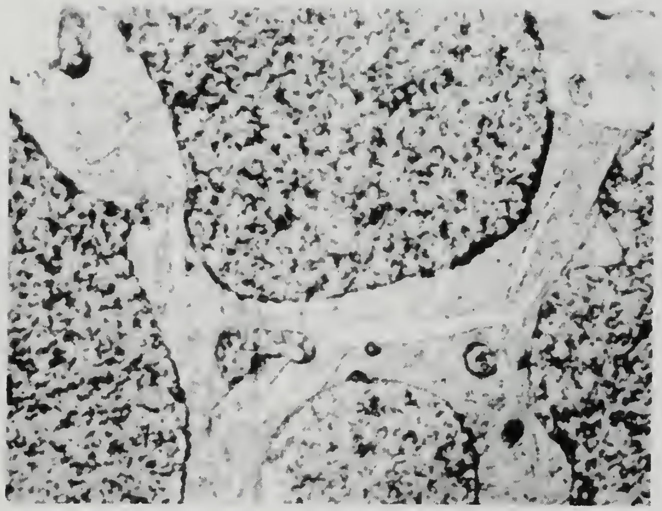
[illegible]

[illegible]

[illegible]



c. (300x)

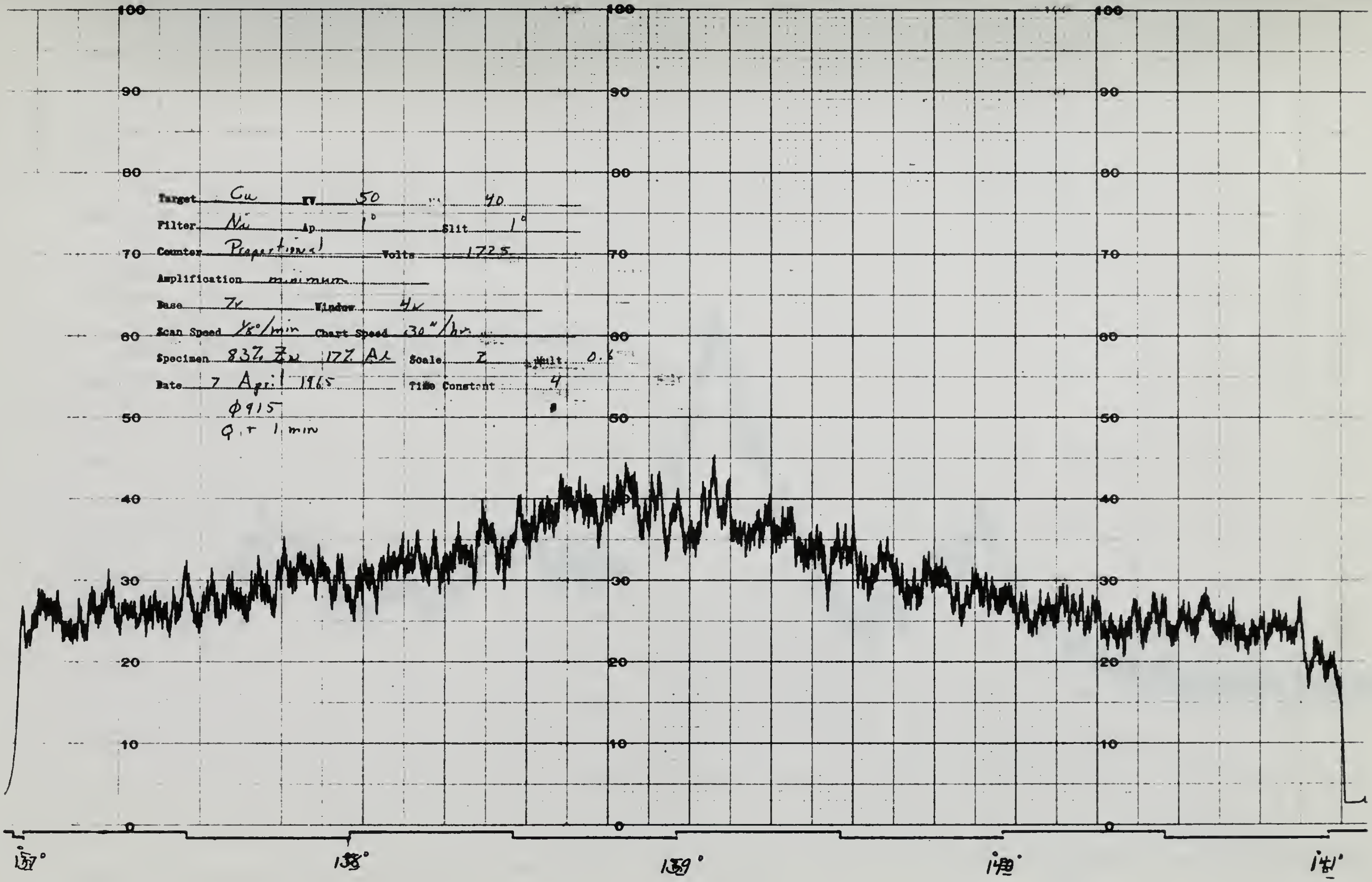


d. (800x)

Fig. I-18 (continued). 23/77 Al-Zn alloy. Micrograph near point where fracture occurred.

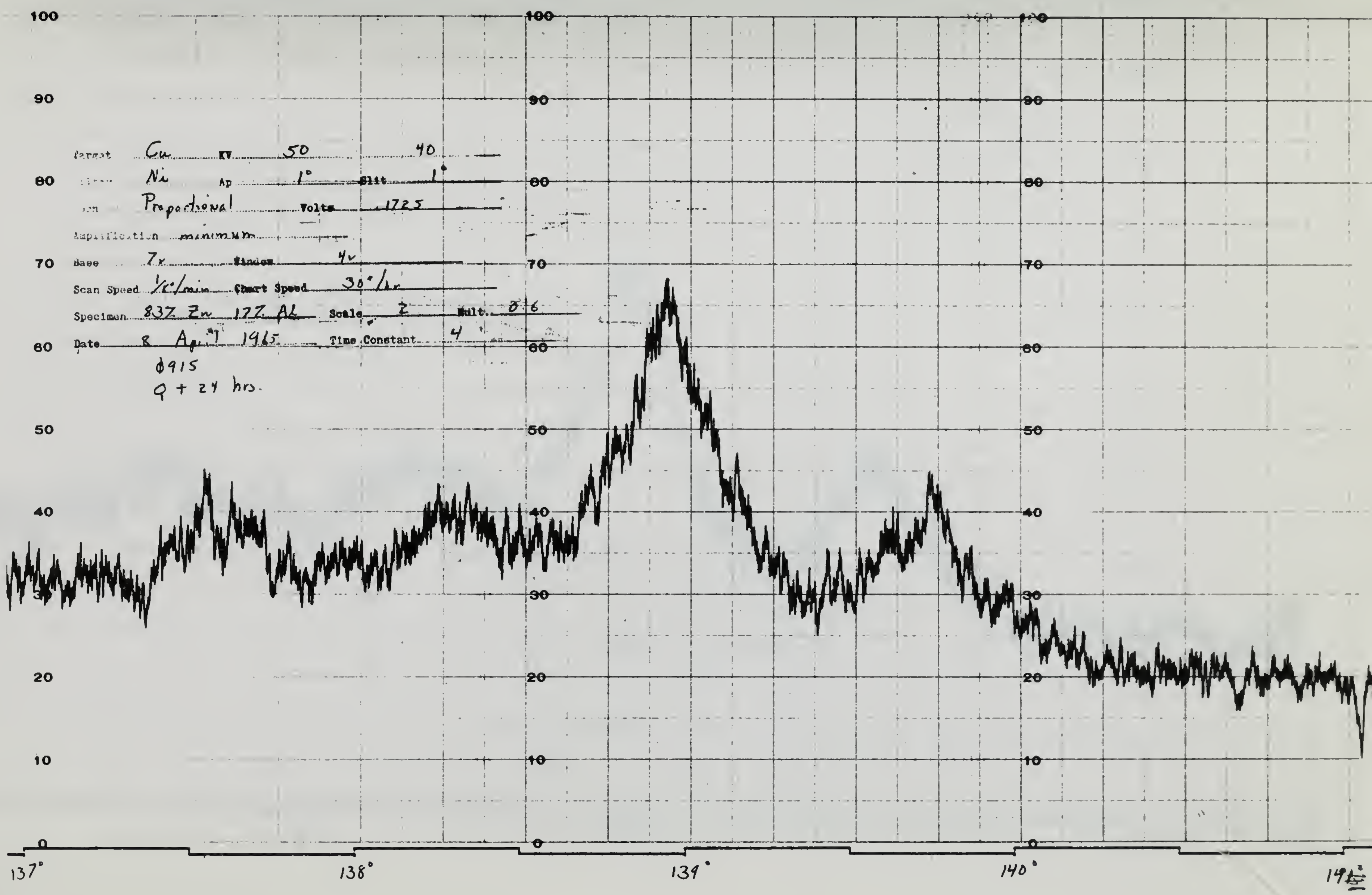
APPENDIX II

X-RAY DIFFRACTOMETER PATTERNS



Target Cu KV 50 40
Filter Ni Ap 1° Slit 1°
Counter Proportional Volts 1725
Amplification minimum
Base 7v Window 4v
Scan Speed 1/8°/min Chart Speed 30"/hr
Specimen 83% Zn 17% Al Scale 2 Mult. 0.6
Date 7 April 1965 Time Constant 4
φ915
Q. + 1 min

Fig. II-1. Diffractometer tracing for 17/83 Al-Zn alloy, Quench plus 1 minute to quench plus 33 minutes.



Target Cu KV 50 40

Filter Ni Ap 1° Slit 1°

Counter Proportional Volts 1725

Amplification minimum

Base 7v Window 4v

Scan Speed 1/8°/min Chart Speed 30°/hr

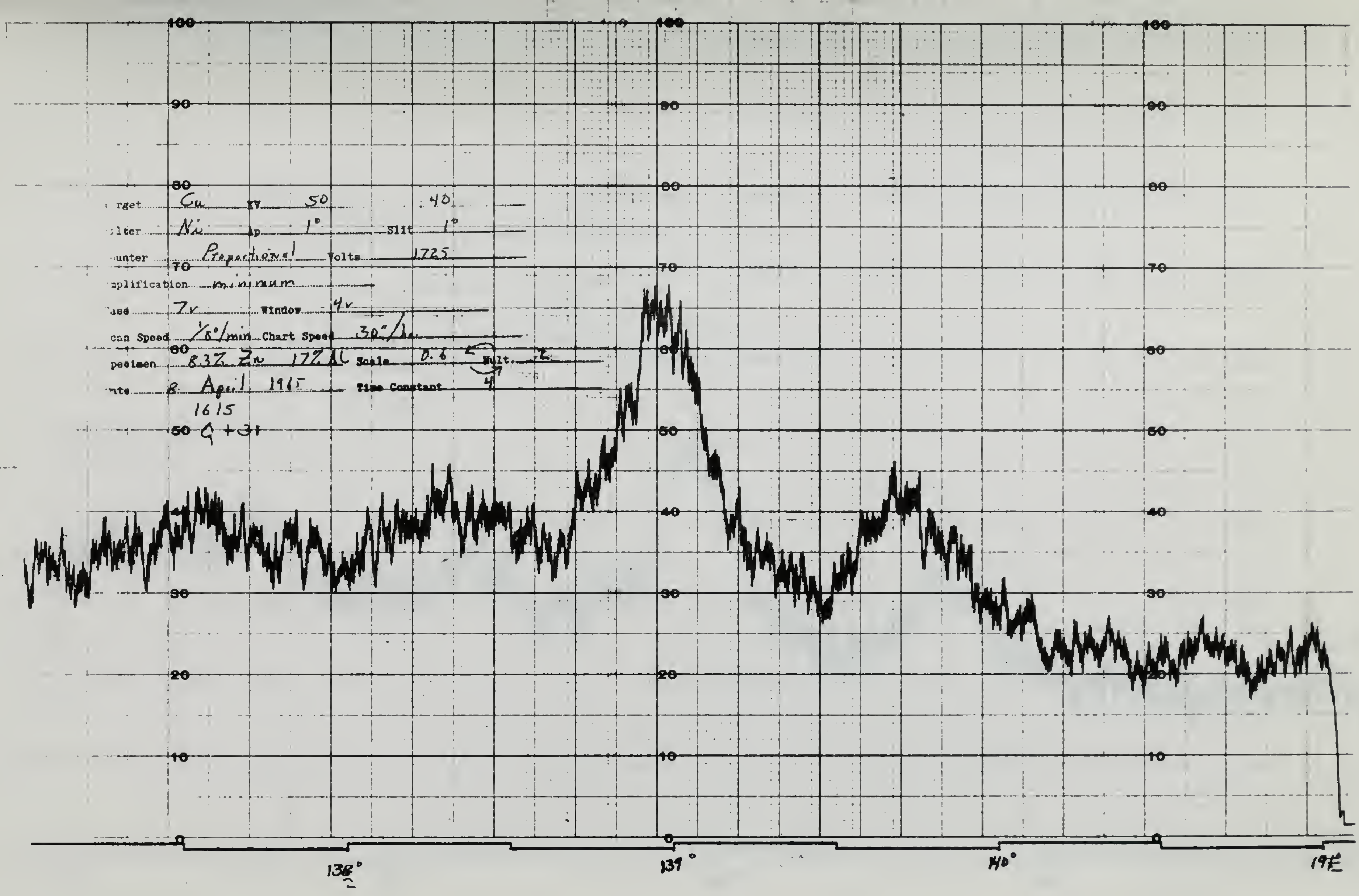
Specimen 83% Zn 17% Al Scale 2 Mult. 0.6

Date 8 April 1965 Time Constant 4

0915

Q + 24 hrs.

Fig. [illegible] Diffractometer tracing for [illegible] Quench [illegible] hours



rget Cu KV 50 40

lter Ni ↓D 1° Slit 1°

unter Proportional Volts 1725

nplification minimum

ase 7v Window 4v

can Speed 1/8°/min Chart Speed 30"/hr

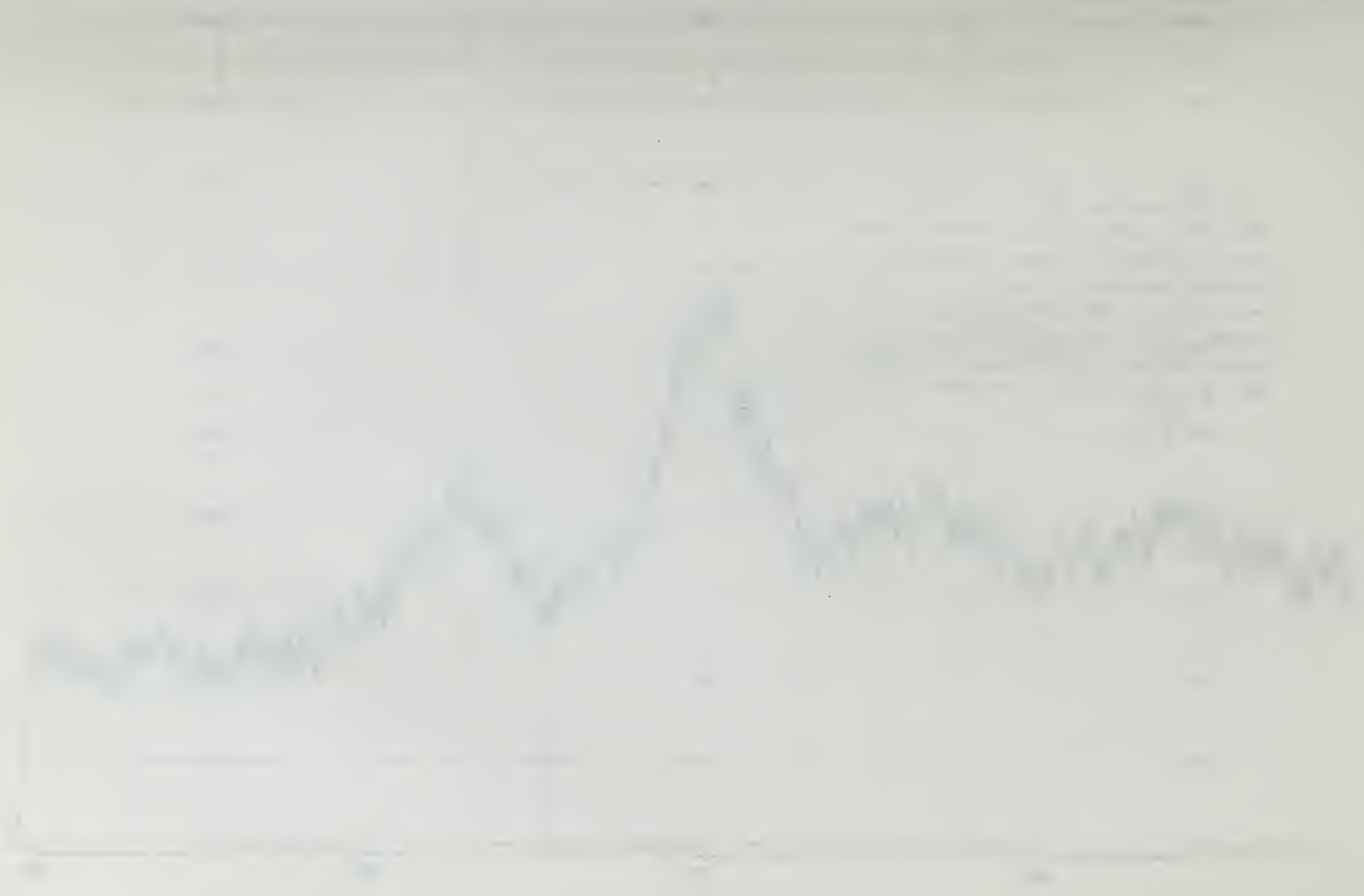
pecimen 83% Zn 17% Al Scale 0.6 Mult. 2

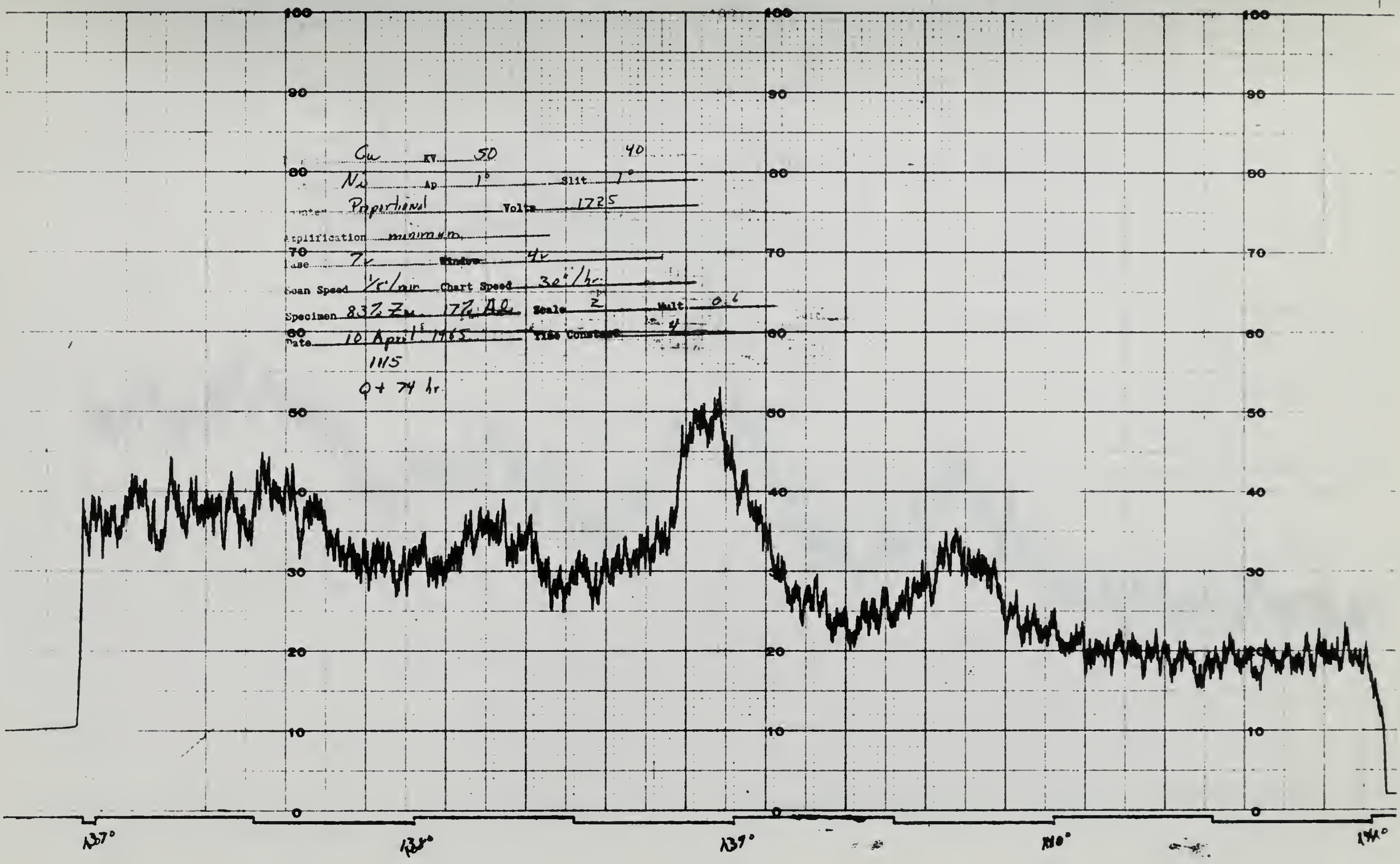
nte 8 April 1965 Time Constant 4

1615

Q + 31

Fig. [illegible] Diffractometer tracing for [illegible] alloy. [illegible]





Cu KV 50 40

Ni Ap 1° Slit 1°

Counter Proportional Volts 1725

Amplification minimum

Base 7v Window 4v

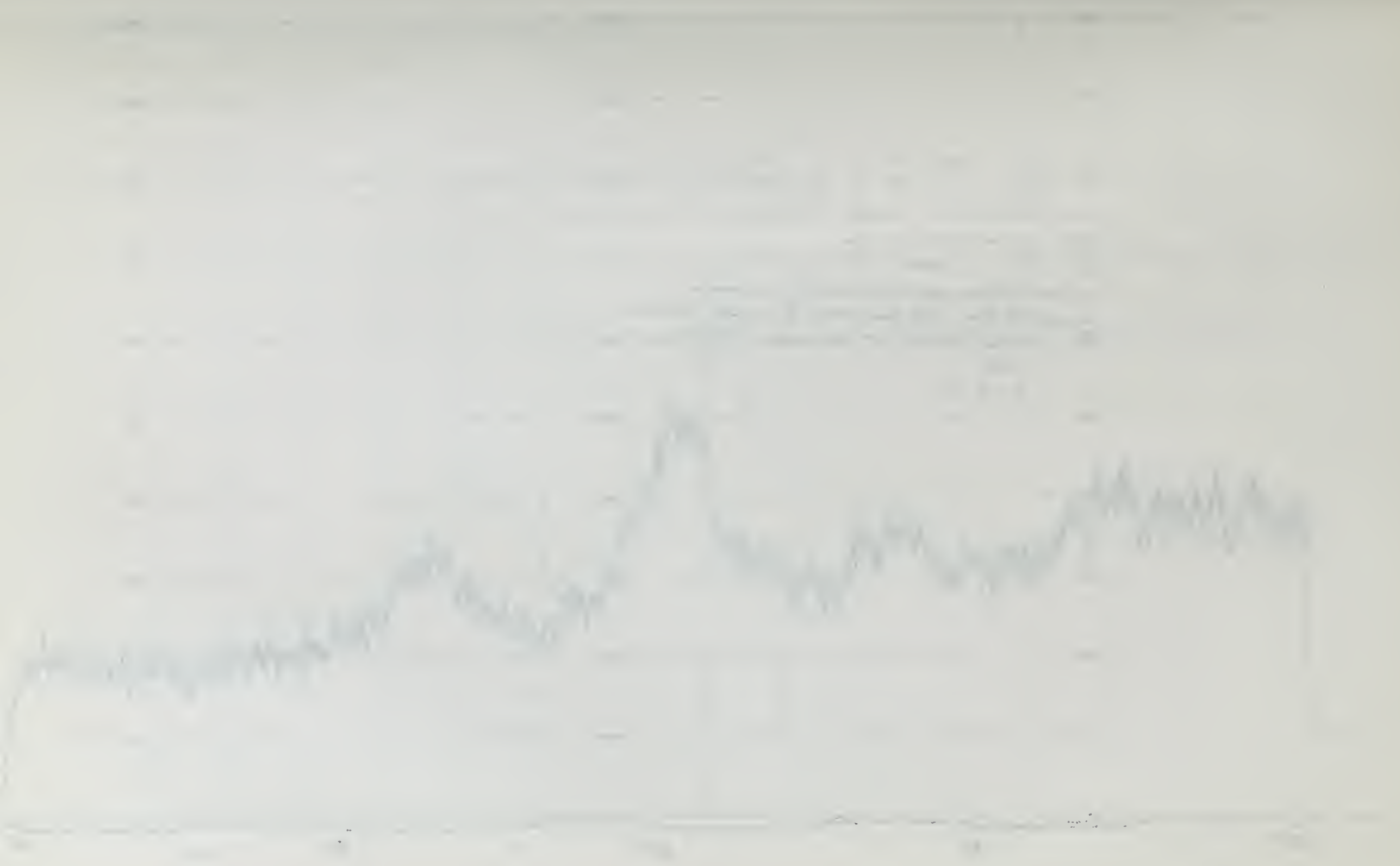
Scan Speed 1/5°/min Chart Speed 30"/hr

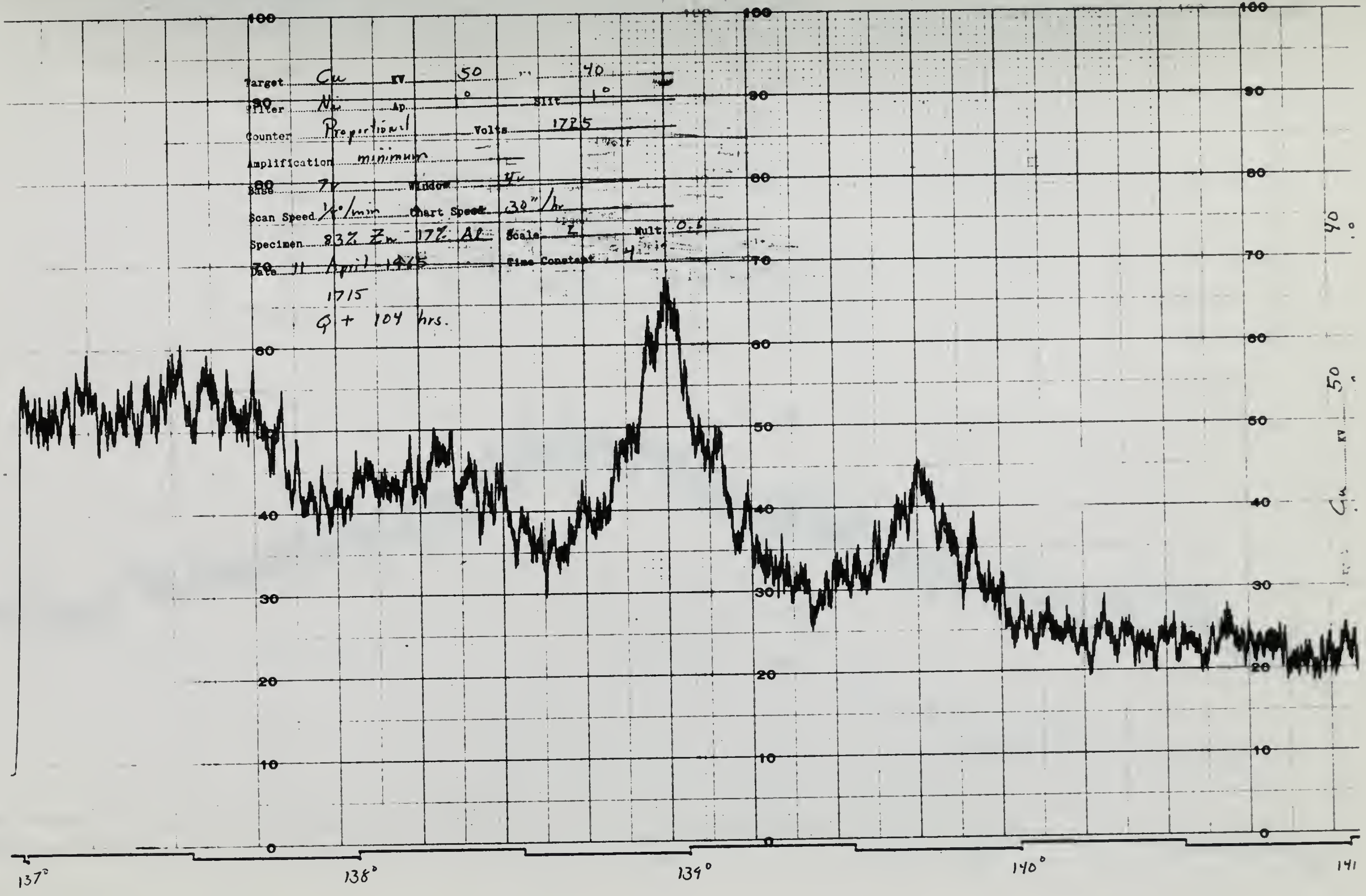
Specimen 83% Zn 17% Al Scale 2 Mult. 0.6

Date 10 April 1965 Time Constant 4

1115

Q + 74 hr

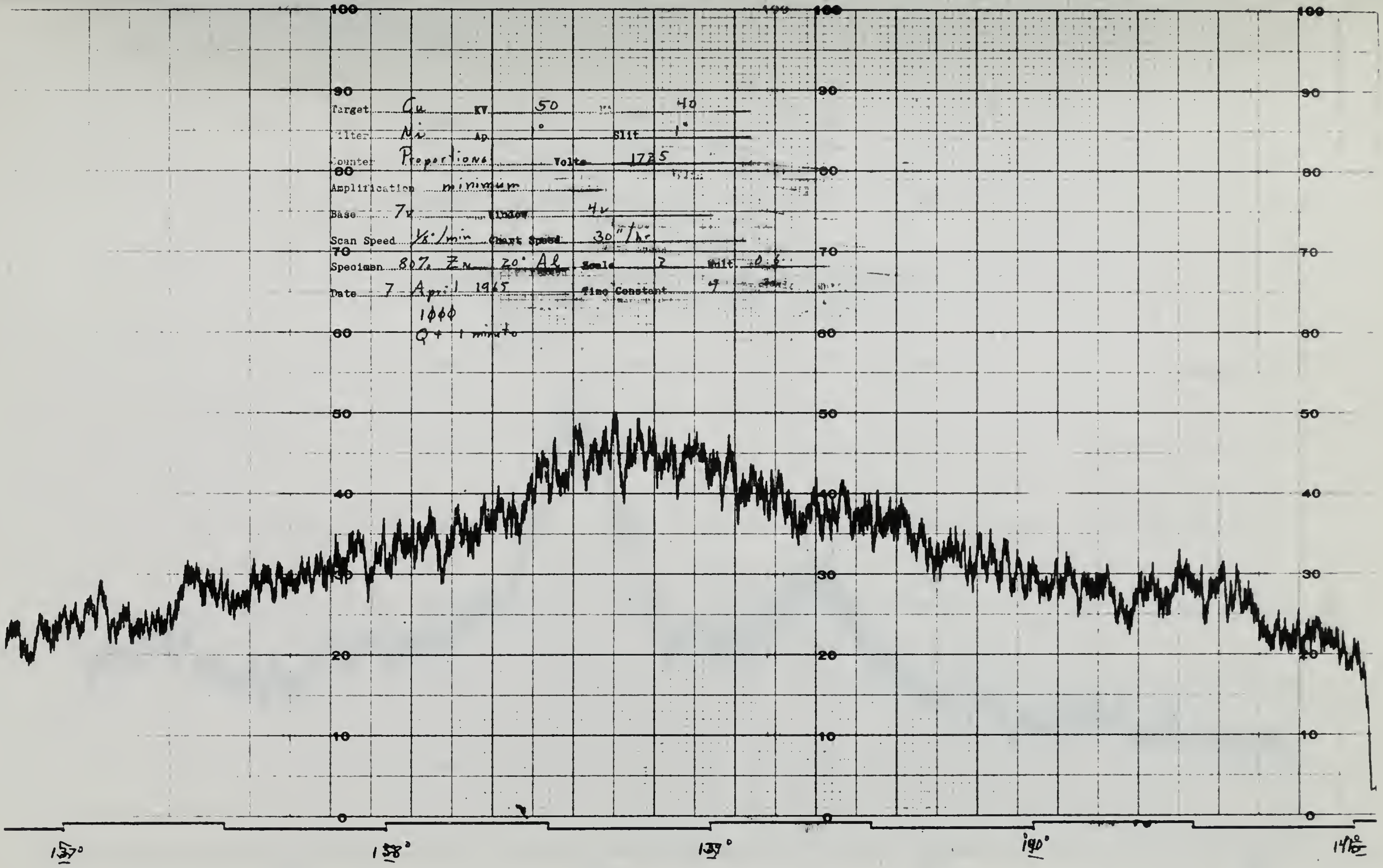




Target Cu KV 50 40
Filter Ni Ap 1° Slit 1°
Counter Proportional Volts 1725
Amplification minimum
Base 7v Window 4v
Scan Speed ½°/min Chart Speed 30"/hr
Specimen 83% Zn 17% Al Scale 2 Mult 0.6
Date 11 April 1965 Time Constant 4

1715
Q + 104 hrs.

[illegible] Di [illegible]



Target Cu KV 50 MA 40

Filter Ni Ap. 1° Slit 1°

Counter Proportional Volts 1735

Amplification minimum

Base 7v Window 4v

Scan Speed 1/8°/min Chart Speed 30"/hr

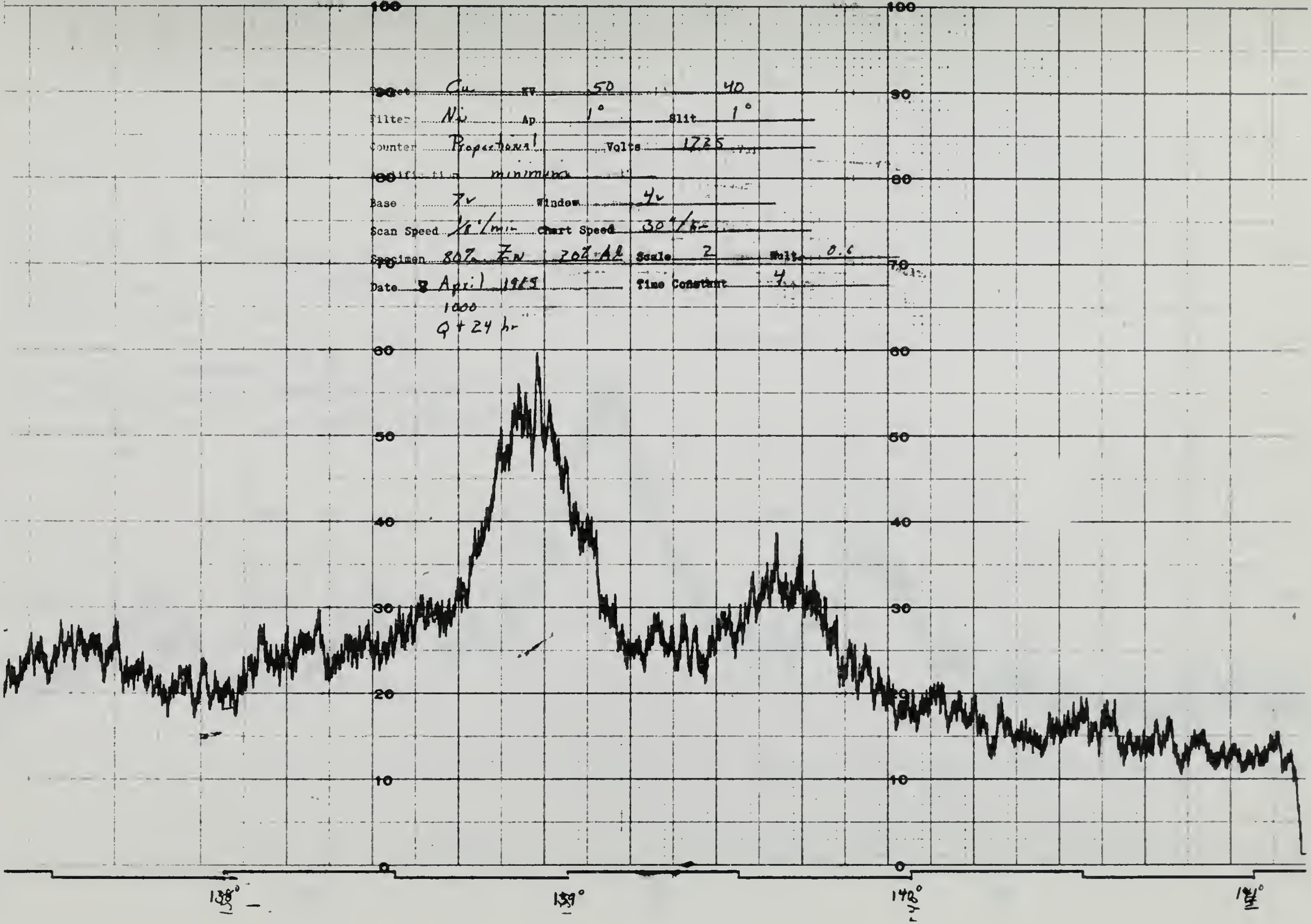
Specimen 80% Zn 20% Al Scale 2 Mult. 0.6

Date 7 April 1965 Time Constant 4

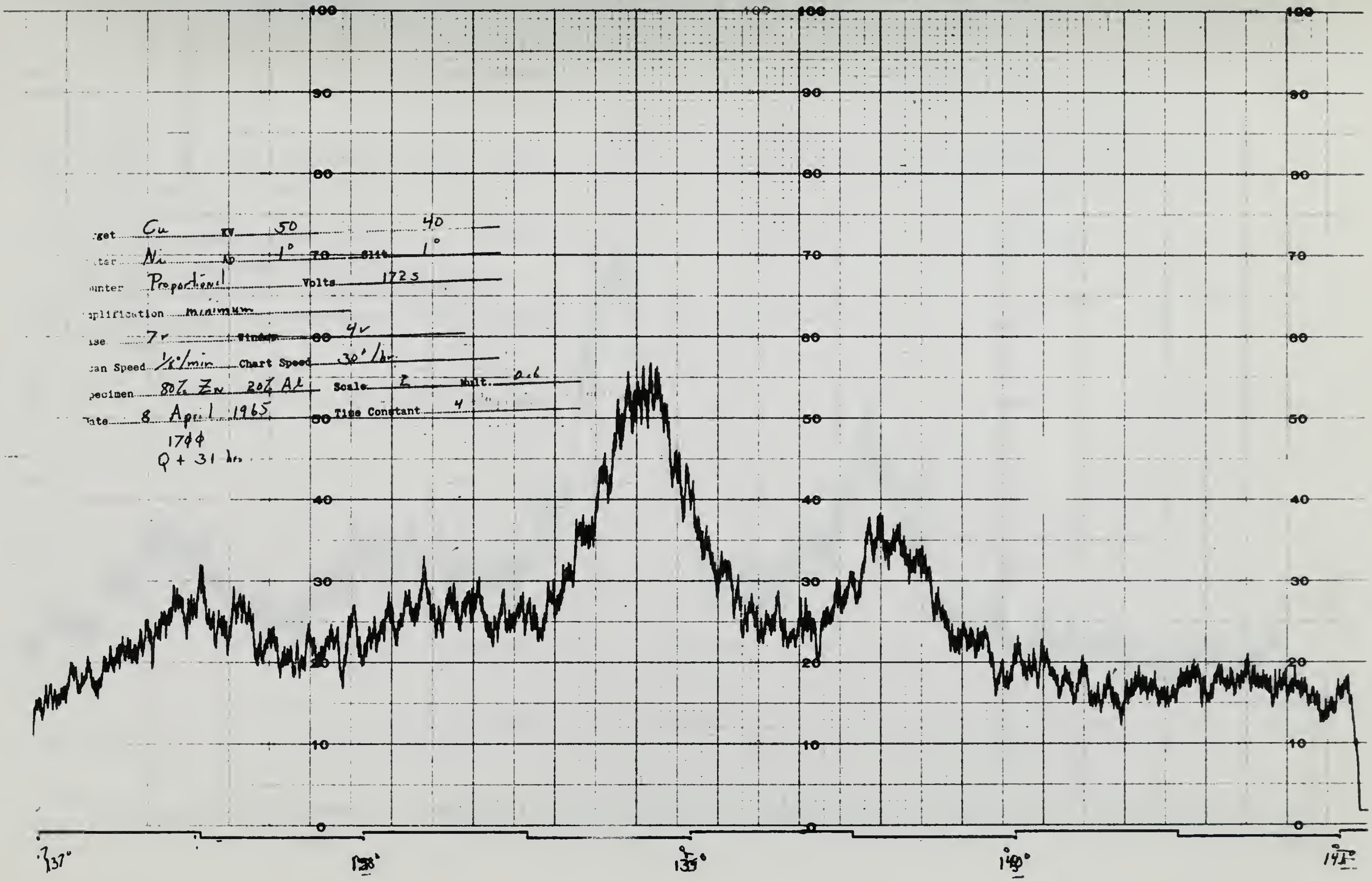
1000

Q + 1 minute

[illegible] plus [illegible]

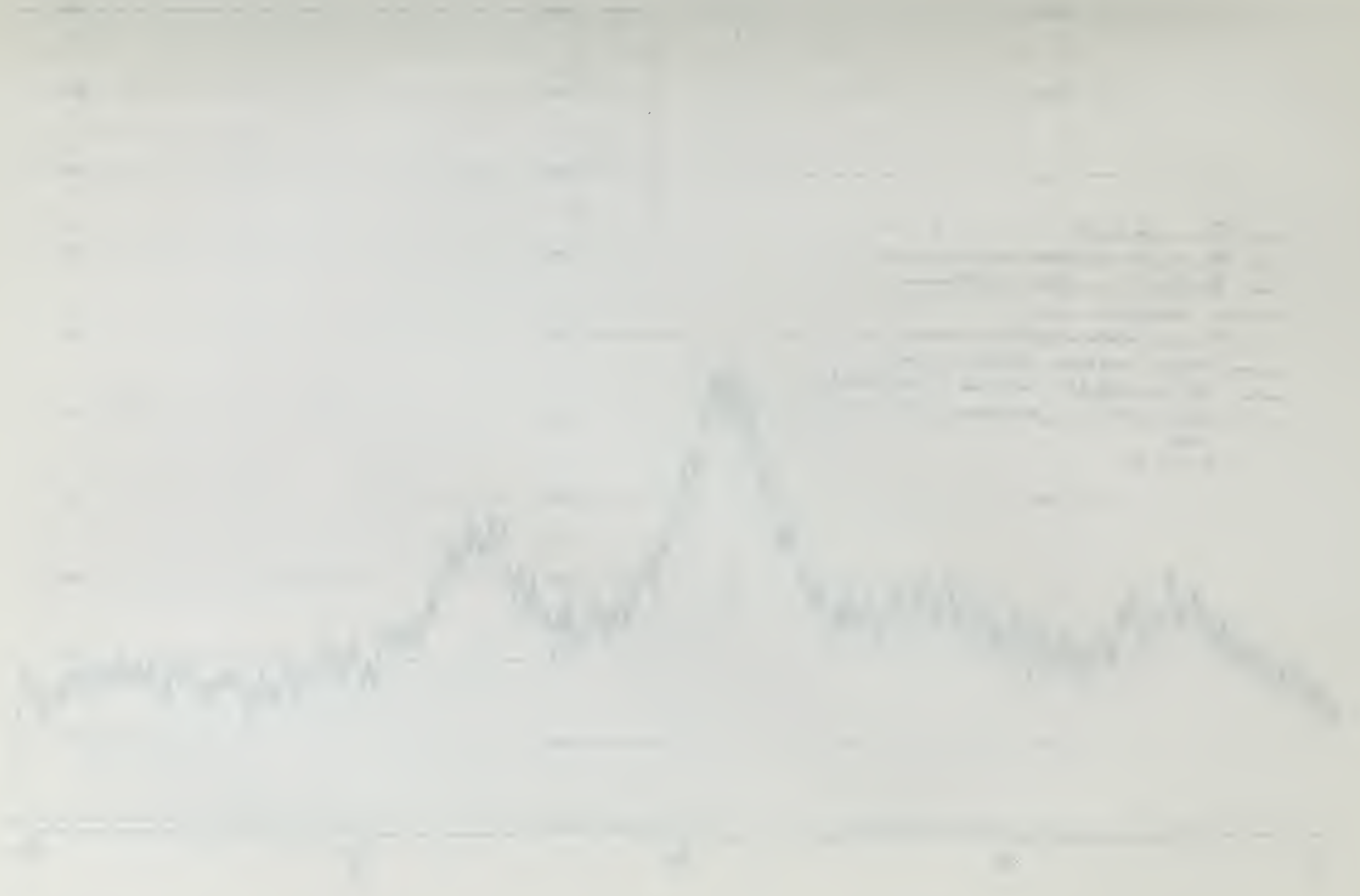


Target Cu KV 50 40
Filter Ni Ap 1° Slit 1°
Counter Proportional Volts 1725
Amplification minimum
Base 7v Window 4v
Scan Speed 1/8°/min Chart Speed 30"/hr
Specimen 80% Zn 20% Al Scale 2 Mult 0.6
Date 8 April 1965 Time Constant 4
1000
Q + 24 hr



get Cu KV 50 40
ter Ni 1° Slit 1°
unter Proportional Volts 1725
plification minimum
se 7v Window 4v
an Speed 1/8°/min Chart Speed 30'/hr
pecimen 80% Zn 20% Al Scale 2 Mult. 0.6
ate 8 April 1965 Time Constant 4
1700
Q + 31 hrs

[illegible] a [illegible]



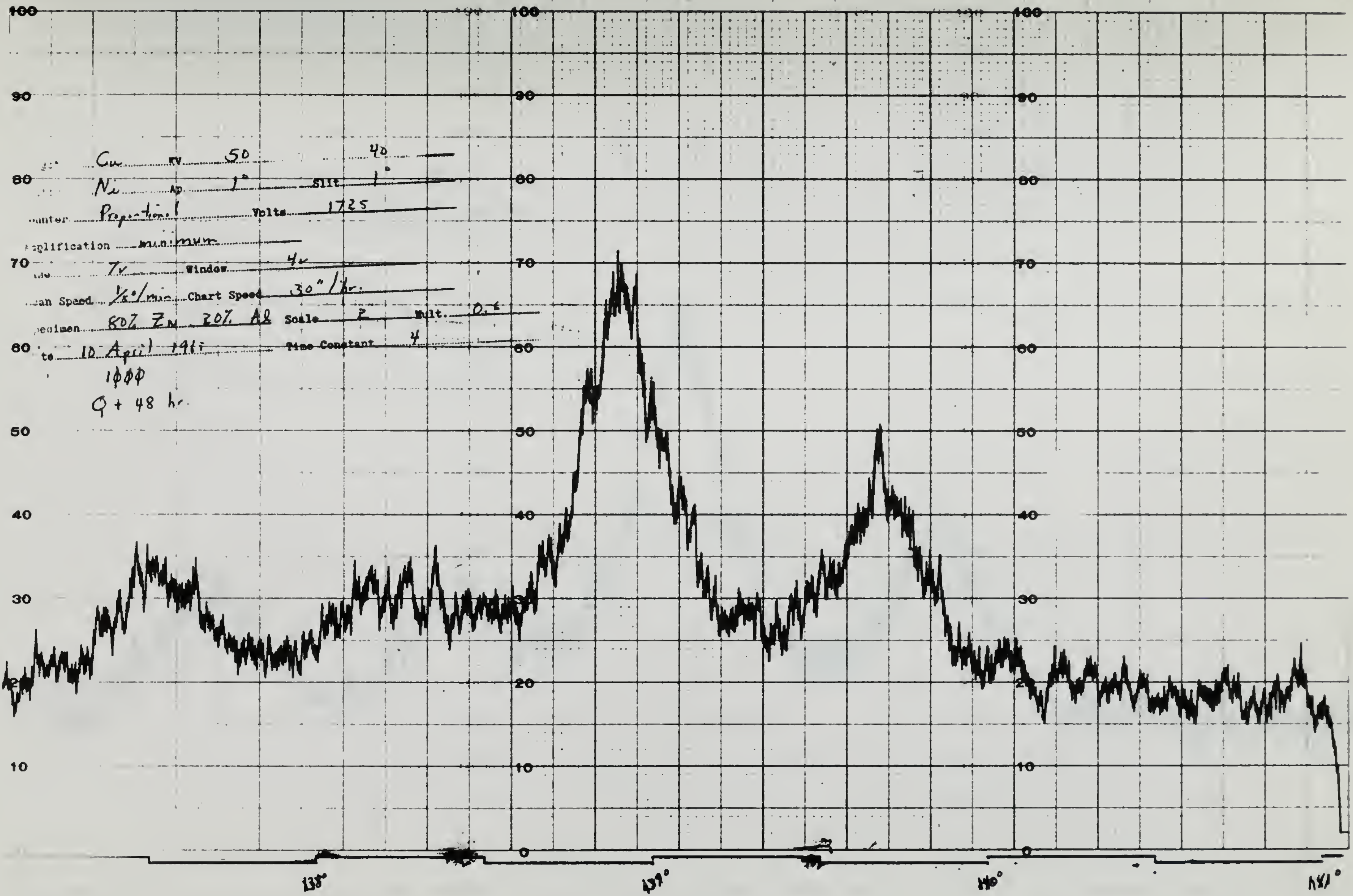
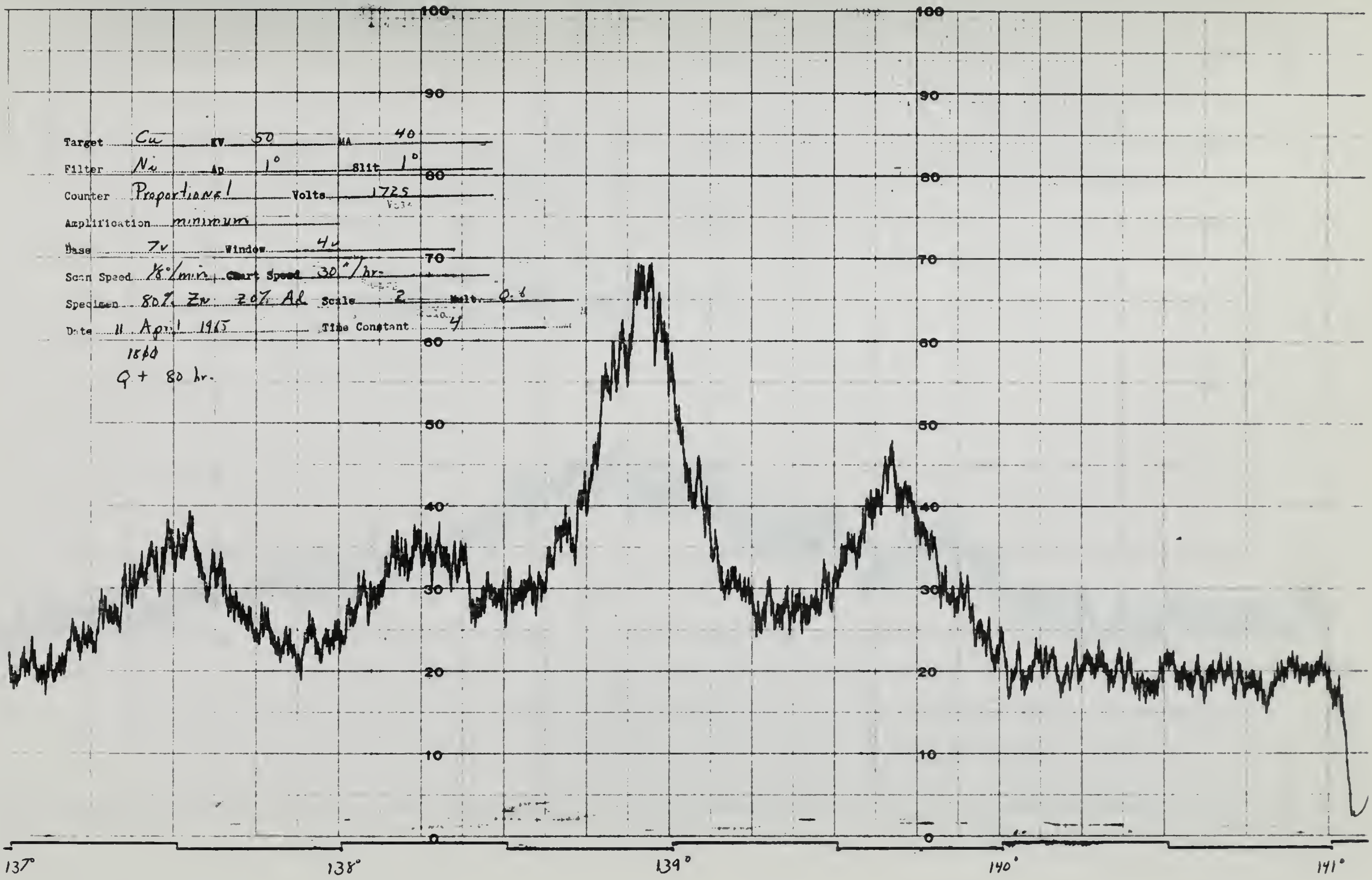
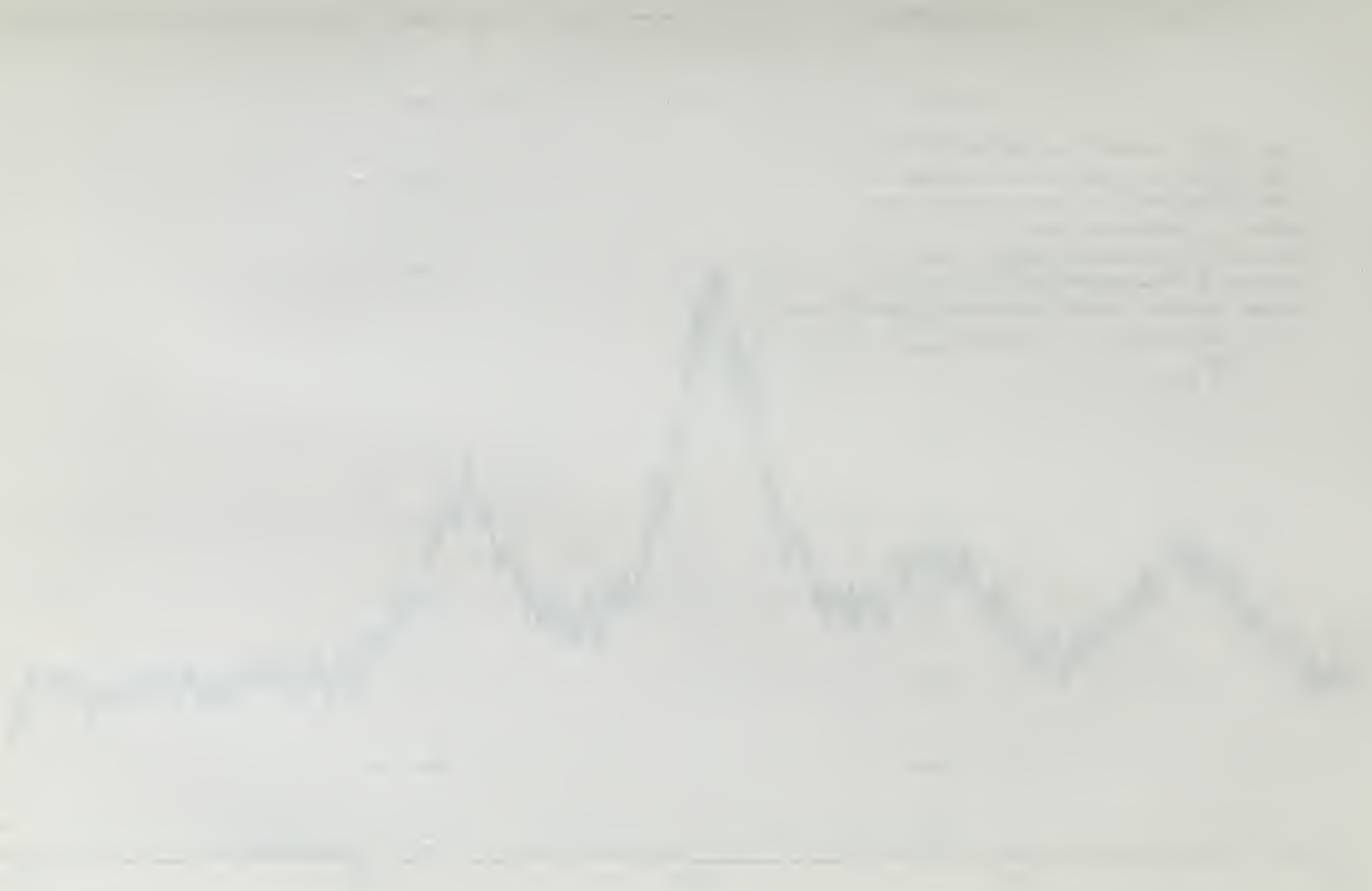
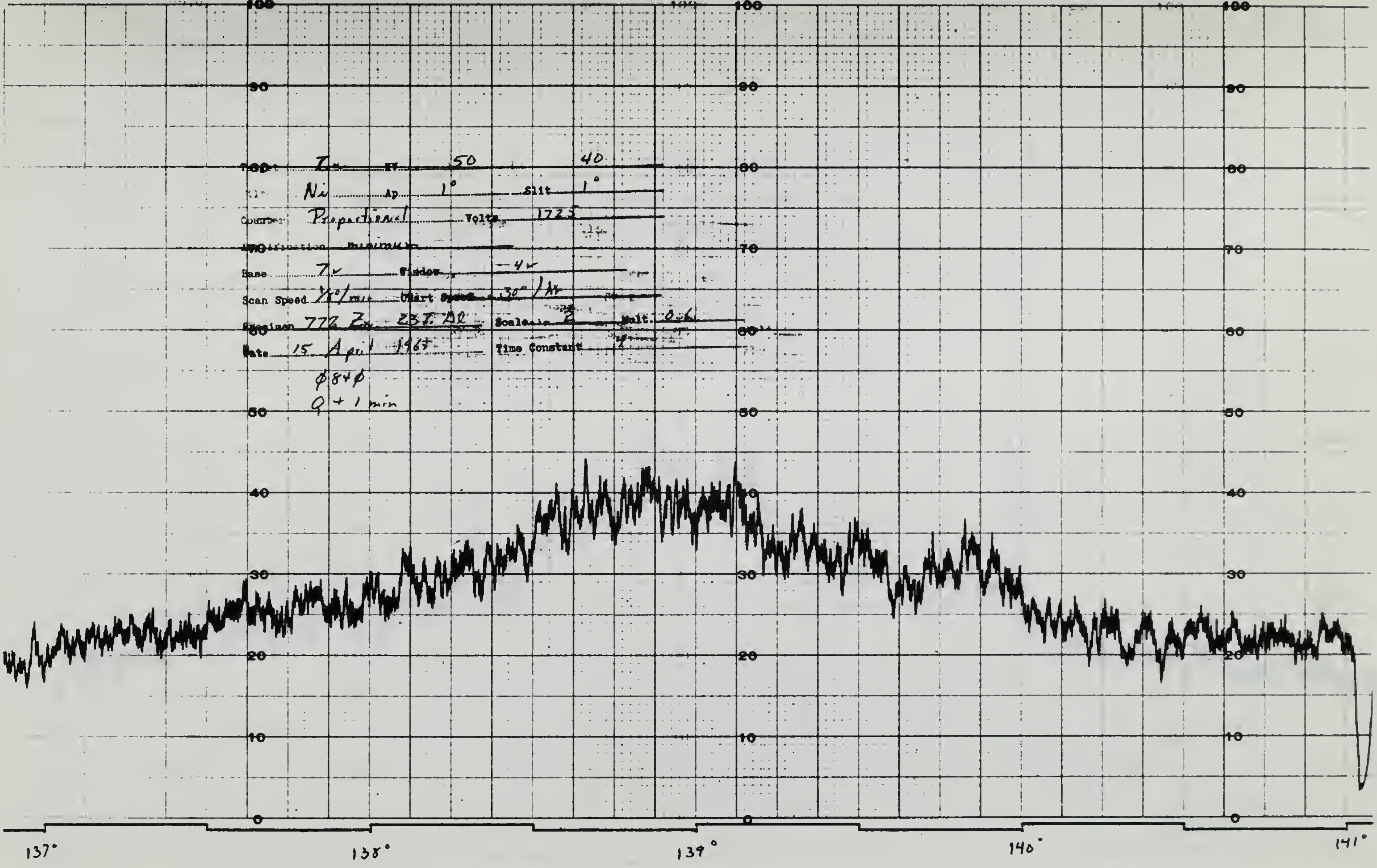


Fig. II-9. Diffractometer tracing for 80Zn-20Al alloy. Quench plus 48 hours.



Target Cu KV 50 MA 40
Filter Ni Ap 1° Slit 1°
Counter Proportional Volts 1725
Amplification minimum
Base 7v Window 4v
Scan Speed 1/8°/min Chart Speed 30"/hr
Specimen 80% Zn 20% Al Scale 2 Mult 0.6
Date 11 April 1965 Time Constant 4
1800
Q + 80 hr.





Target Zn KV 50 40

Filter Ni Ap 1° Slit 1°

Counter Proportional Volts 1725

Amplification minimum

Base 7v Window 4v

Scan Speed 1/8°/min Chart Speed 30"/hr

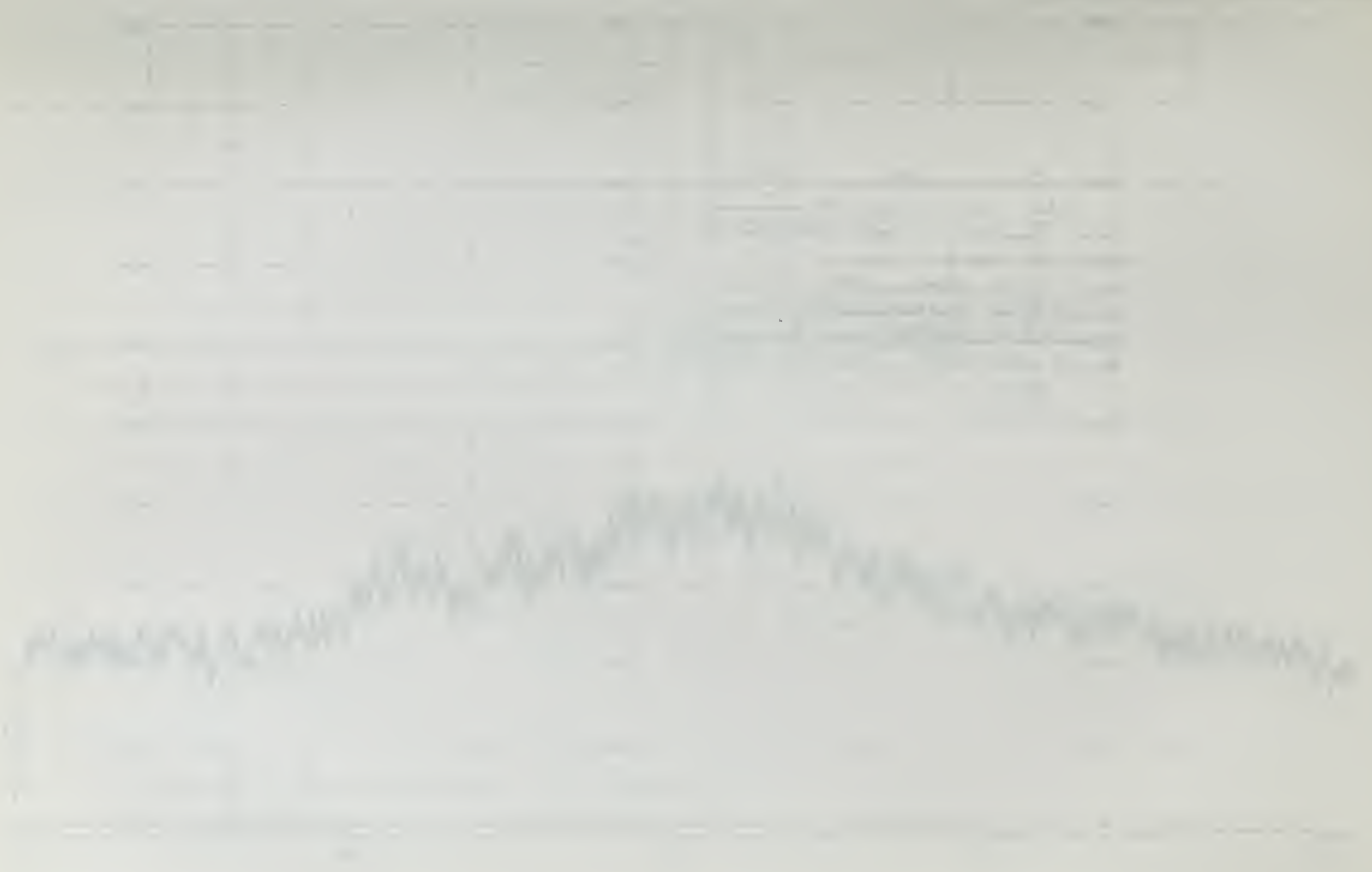
Specimen 772 Zn - 23% Al Scale 2 Mult. 0.6

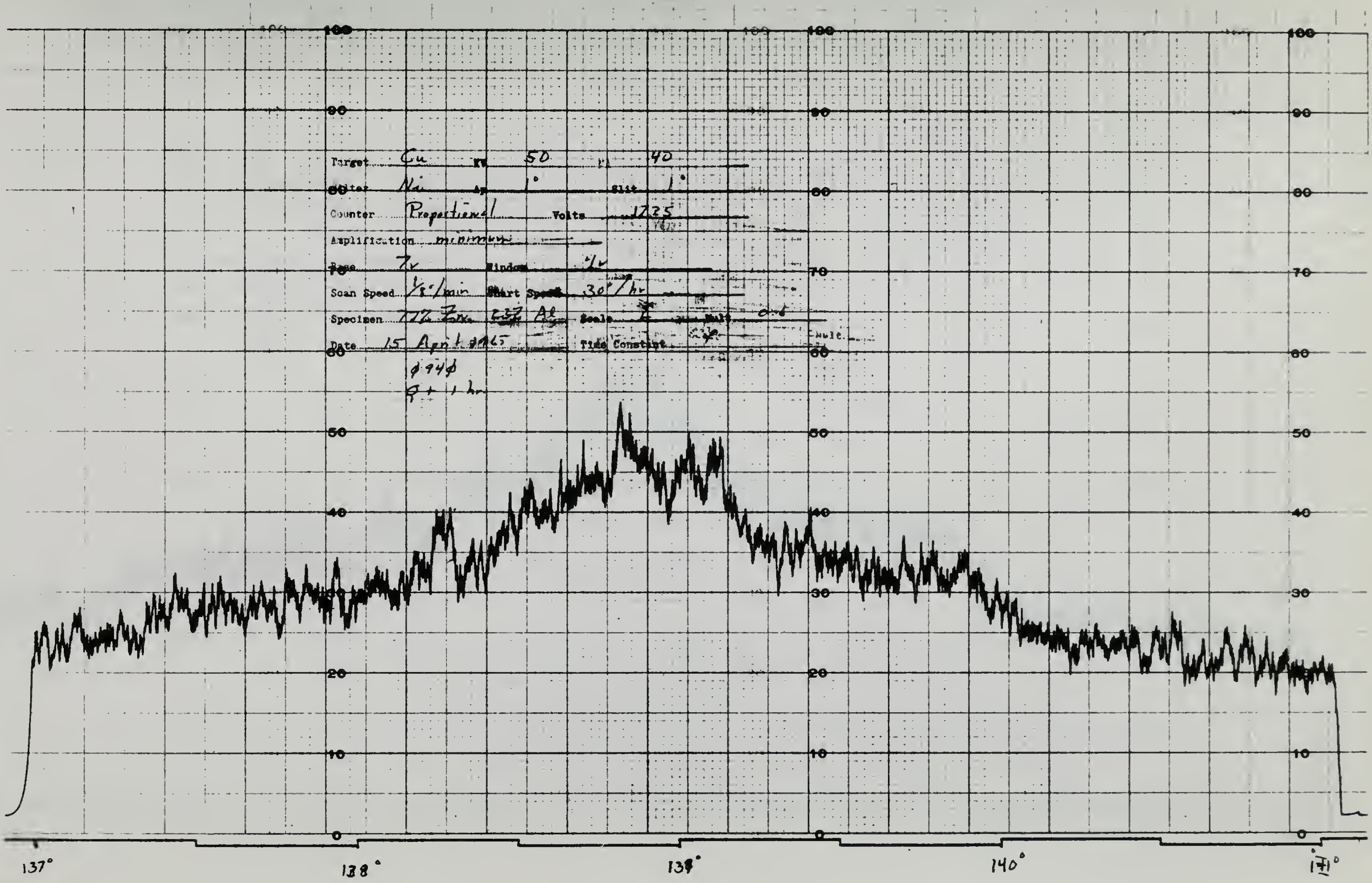
Date 15 April 1965 Time Constant 4

ø840

Q + 1 min

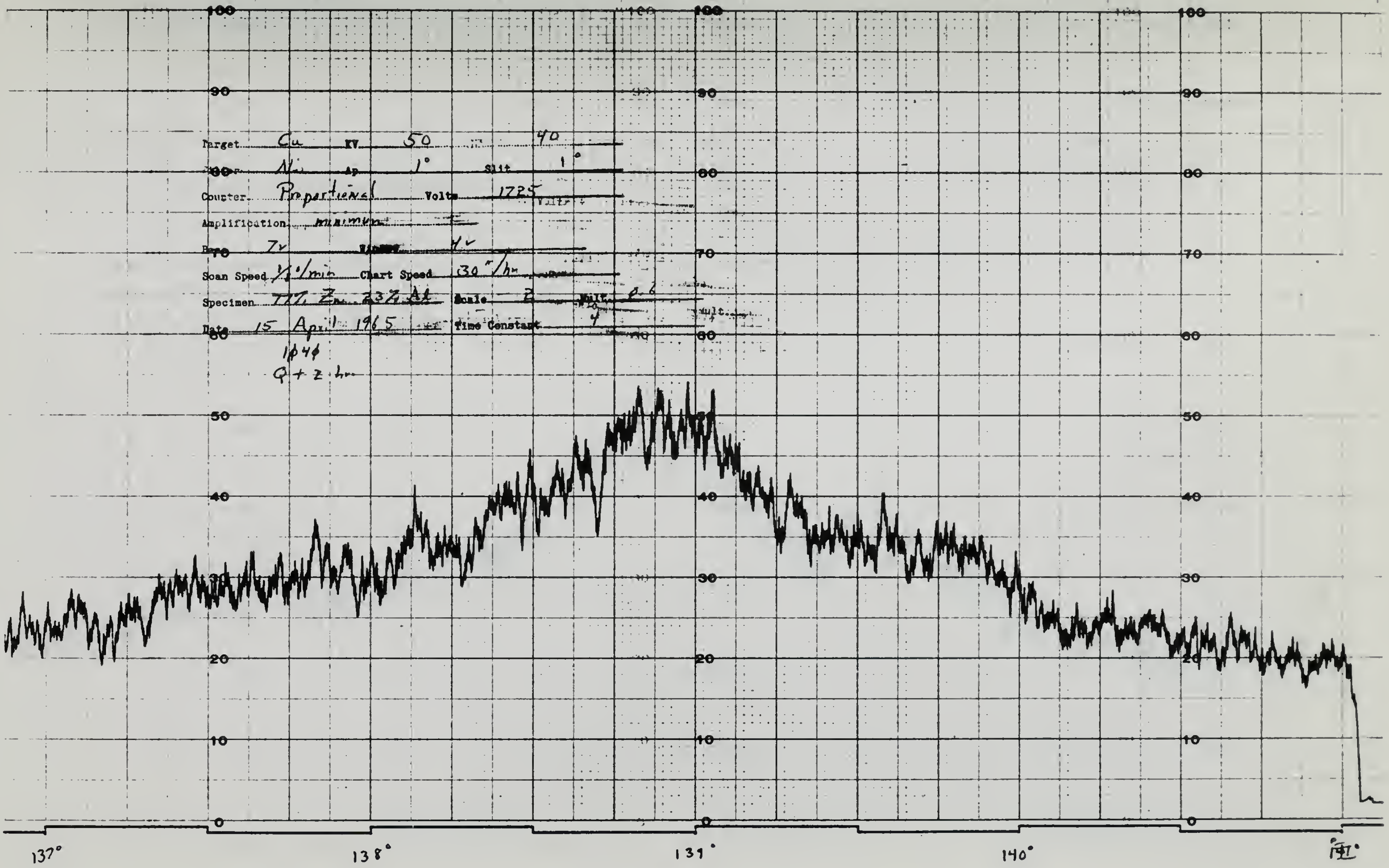
Fig. [illegible]. Diffractometer tracing for [illegible] Zn alloy. Quench plus 1 minute.





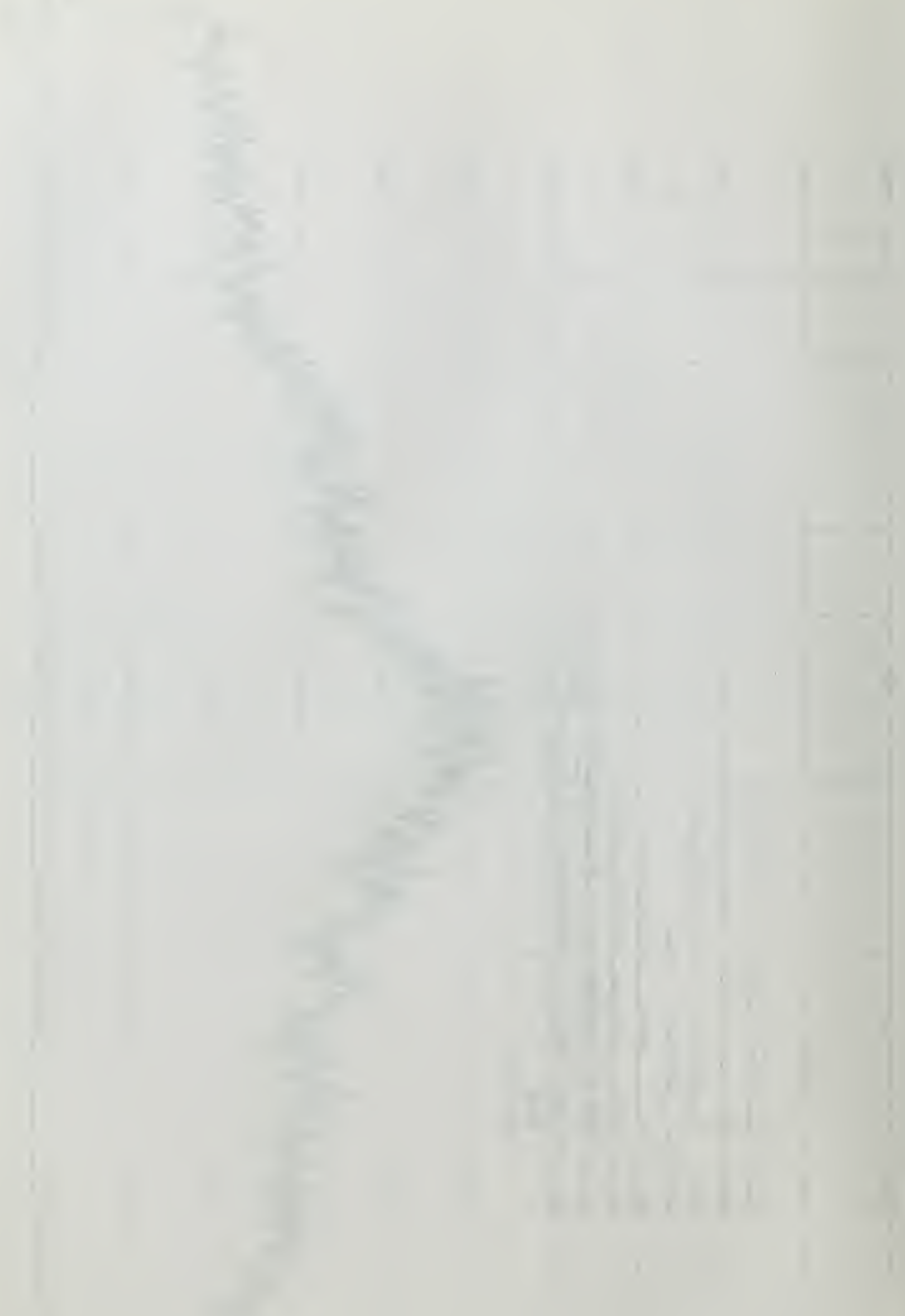
Target Cu KV 50 MA 40
Filter Ni Ap 1° Slit 1°
Counter Proportional Volts 1725
Amplification minimum
Base 7v Window 4v
Scan Speed 1/8°/min Chart Speed 30"/hr
Specimen 77% Zn 23% Al Scale Mult 0.6
Date 15 April 1965 Time Constant
0940
Q + 1 hr

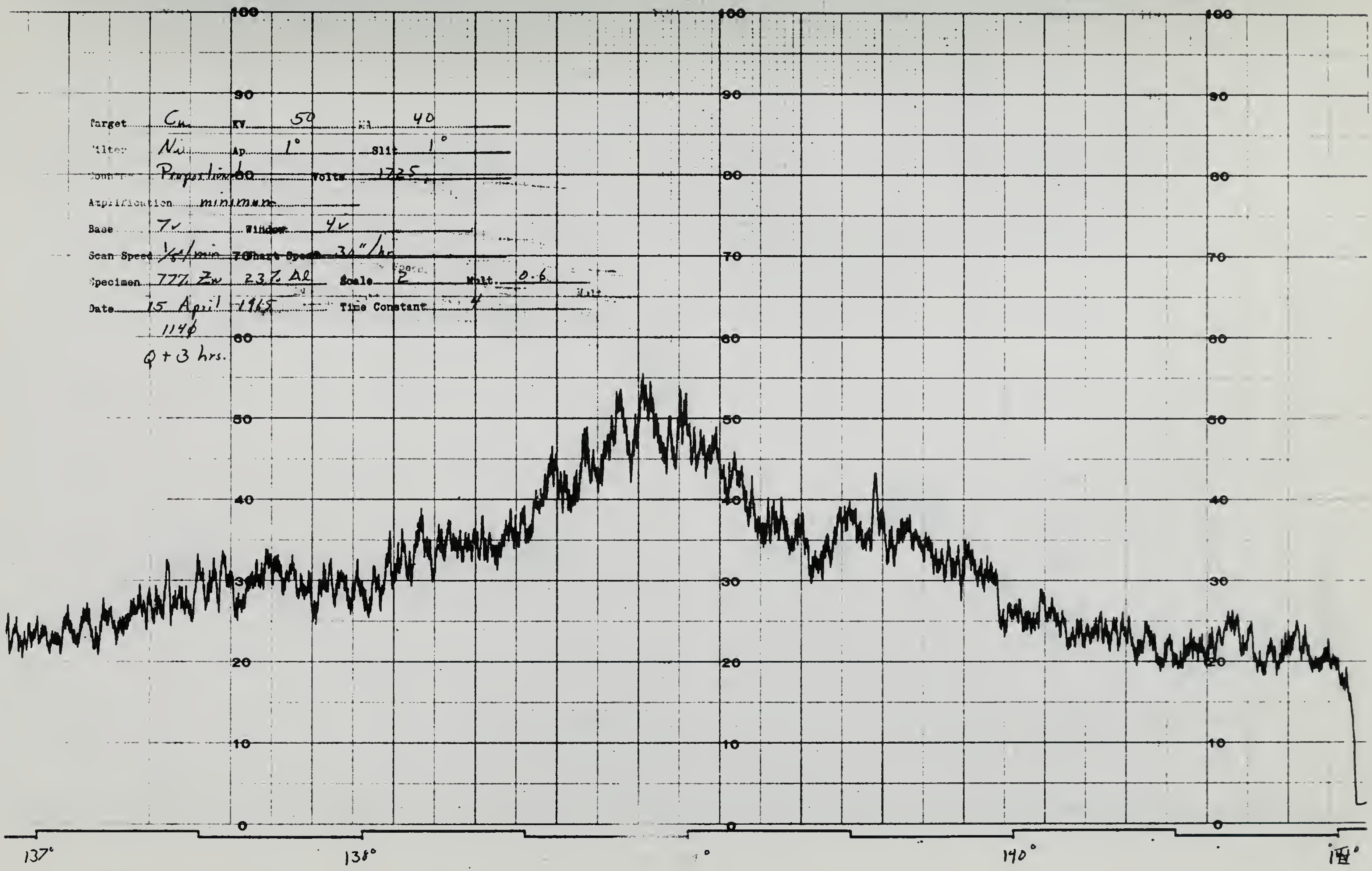
Fig. II-12. Diffractometer tracing for 23/77 Al-Zn alloy. Quench plus 1 hour



Target Cu KV 50 40
Ni Ap 1° Slit 1°
Counter Proportional Volts 1725
Amplification minimum
7v 4v
Scan Speed 1/2°/min Chart Speed 30"/hr
Specimen 77% Zn 23% Al Scale 2 Mult. 0.6
Date 15 April 1965 Time Constant 4
1040
Q + 2 hr

Fig. [illegible]. Diffractometer tracing for [illegible] (quench plus 2 hours)





Target Cu KV 50 MA 40

Filter Ni Ap. 1° Slit 1°

Counter Proportional Volts 1725

Amplification minimum

Base 7v Window 4v

Scan Speed 1/8°/min Chart Speed 30"/hr

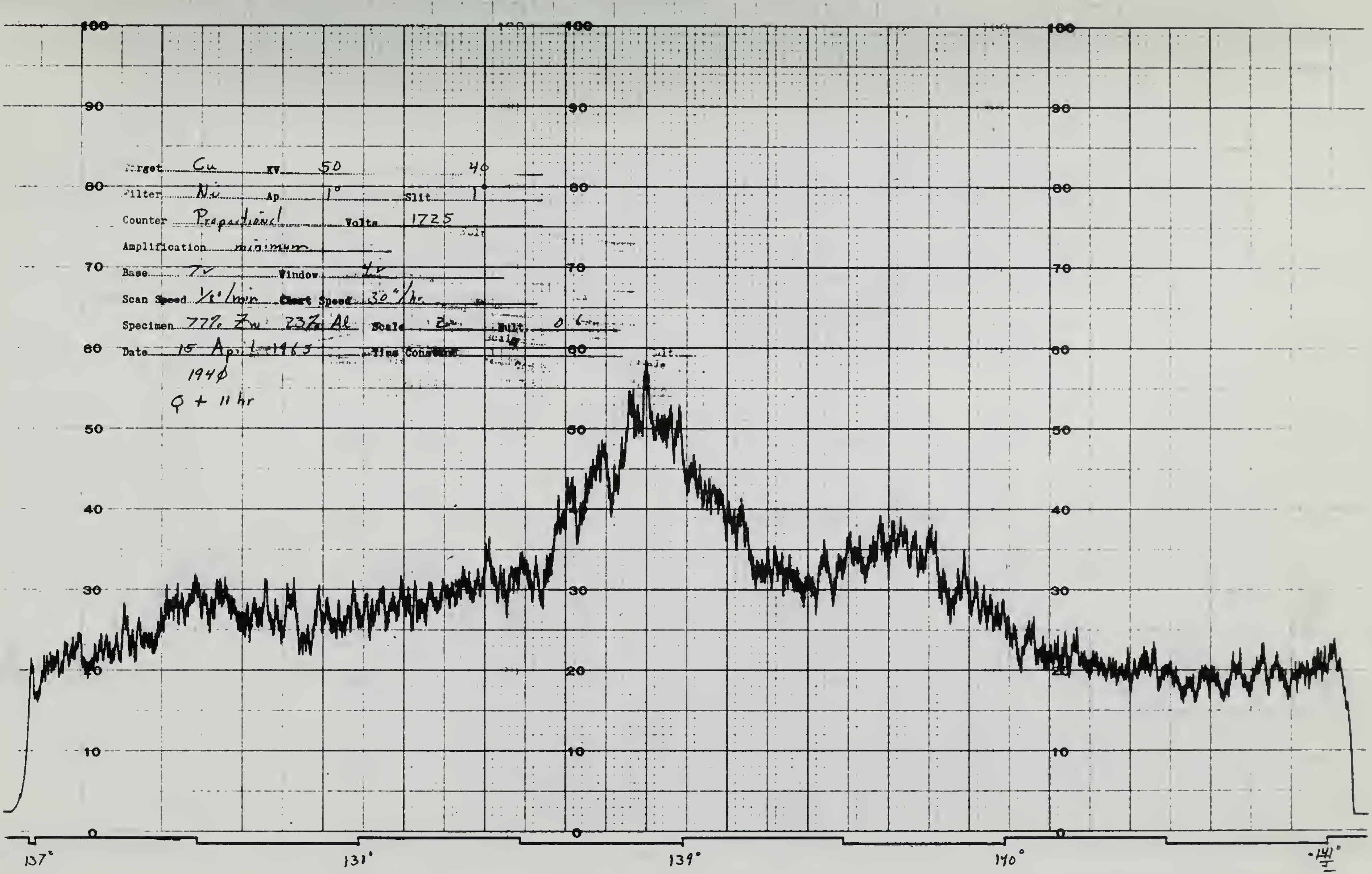
Specimen 77% Zn 23% Al Scale 2 Mult. 0.6

Date 15 April 1965 Time Constant 4

1140

Q + 3 hrs.

Fig. II-14. Diffractometer tracing for 77/23 Al-Zn alloy. Quench plus 3 hours.



Target Cu KV 50 40

Filter Ni Ap 1° Slit 1

Counter Proportional Volts 1725

Amplification minimum

Base 7v Window 4v

Scan Speed ½°/min Chart Speed 30"/hr

Specimen 77% Zn 23% Al Scale Mult. 0.6

Date 15 April 1965 Time Constant

1940

Q + 11 hr

Fig. [illegible]. Diffractometer tracing for 23% Al-Zn alloy. Quench plus 11 hours.

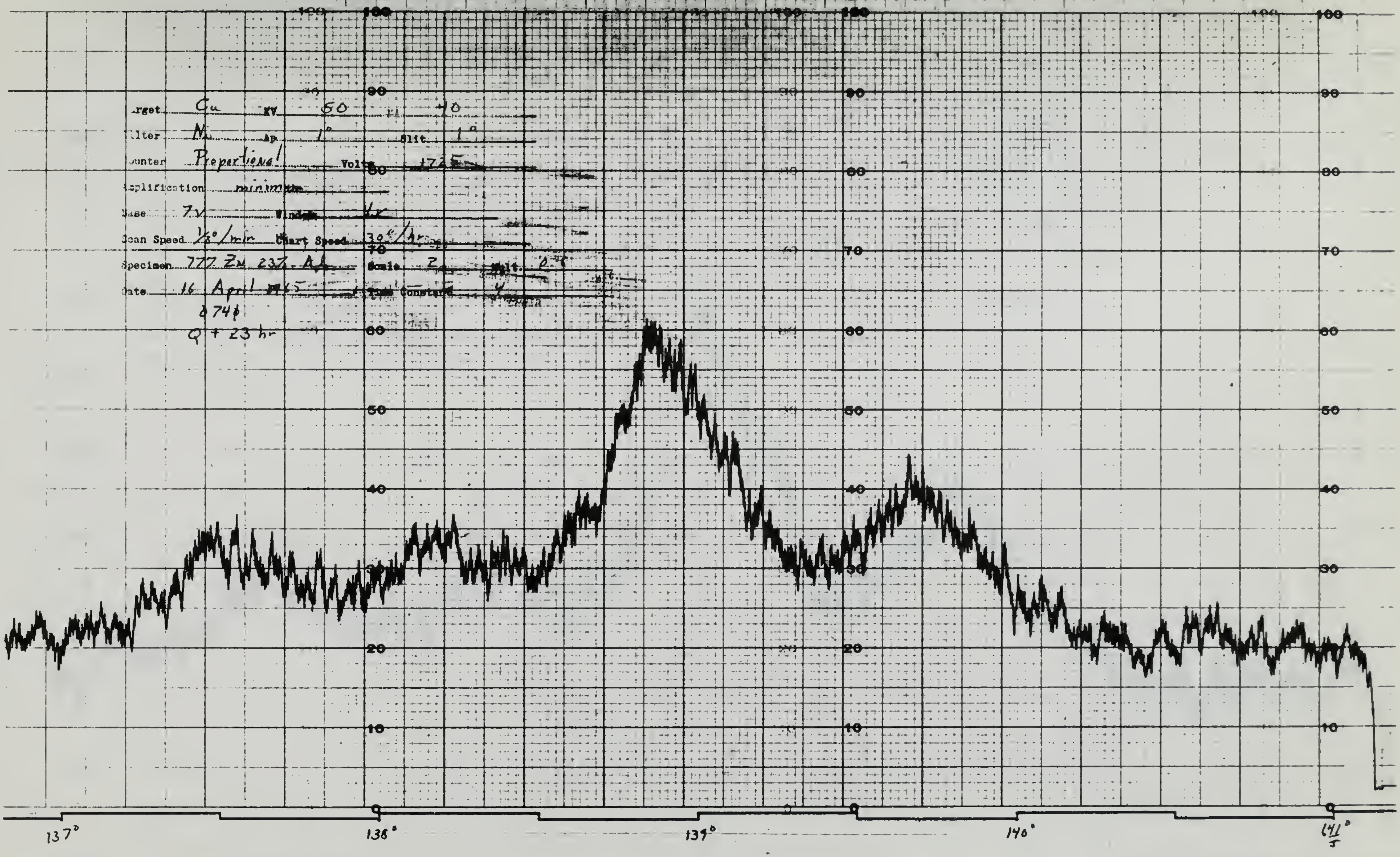
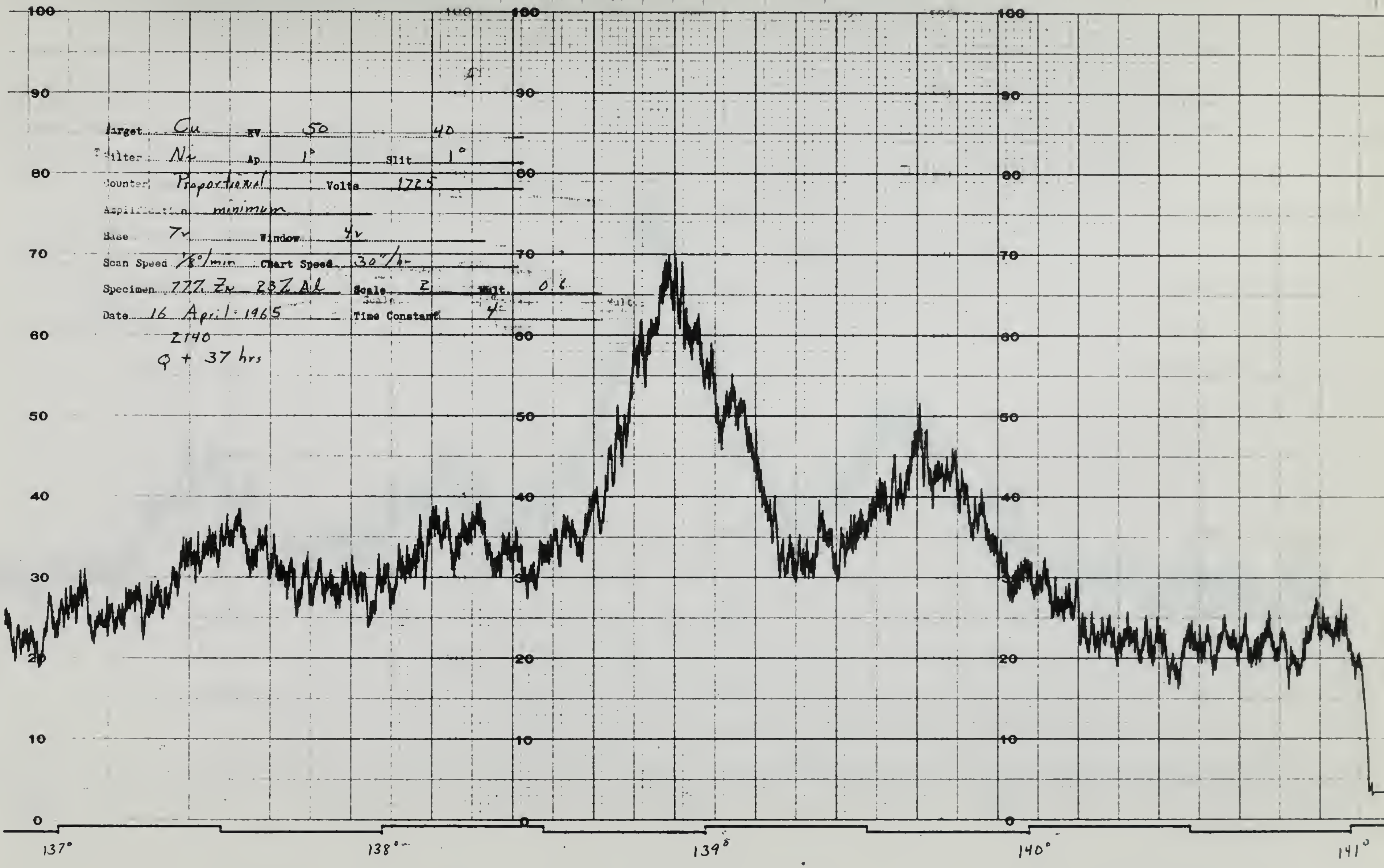


Fig. II-16. Diffractometer tracing for 23/77 Al-Zn alloy. Quench plus 23 hours.



Target Cu KV 50 40
Filter Ni Ap. 1° Slit 1°
Counter Proportional Volts 1725
Amplification minimum
Base 7v Window 4v
Scan Speed 1/8°/min Chart Speed 30"/hr
Specimen 77% Zn 23% Al Scale 2 Mult. 0.6
Date 16 April 1965 Time Constant 4
Z140
Q + 37 hrs

Fig. II-17. Diffractometer tracing for [illegible]

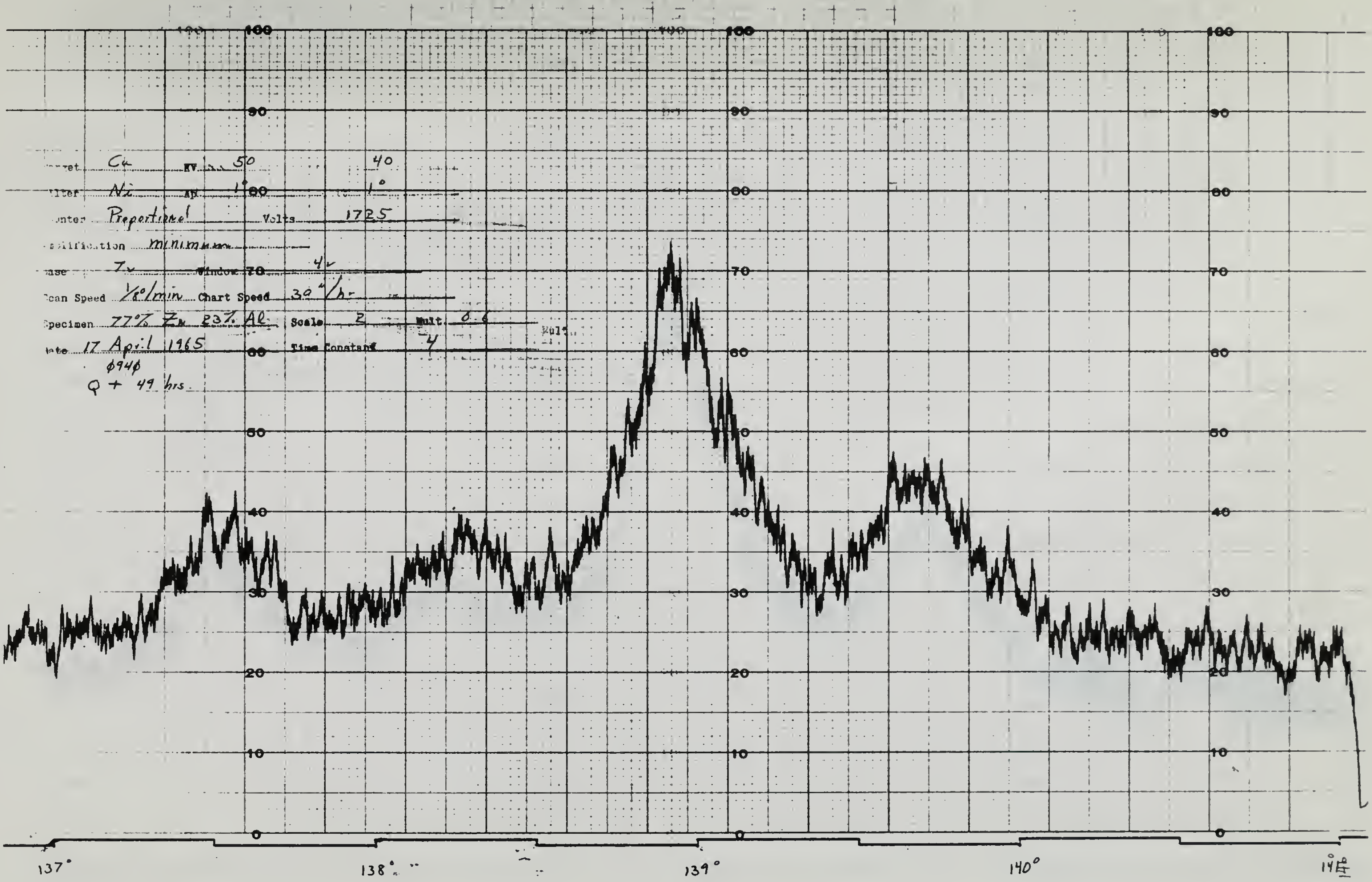
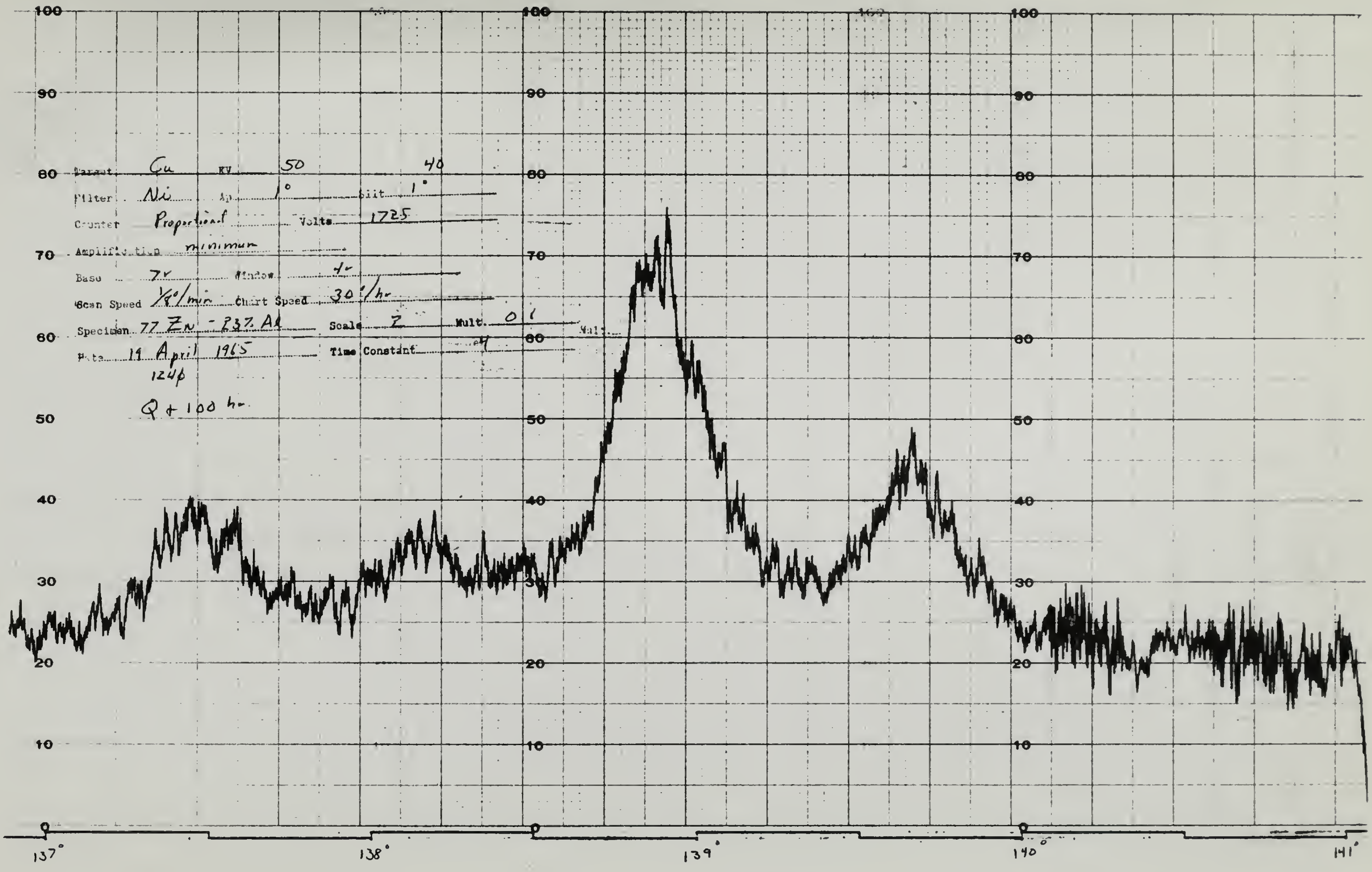


Fig. [illegible]. Diffractometer tracing for 23% Al-Zn alloy. Quench plus 49 hours.


Target Cu KV 50 40
Filter Ni Ap 1° Slit 1°
Counter Proportional Volts 1725
Amplification minimum
Base 7v Window 4v
Scan Speed 1/8°/min Chart Speed 30"/hr
Specimen 77 Zn - 23% Al Scale 2 Mult. 0.1
Date 19 April 1965 Time Constant 4
124p
Q + 100 hr
100
90
80
70
60
50
40
30
20
10
0
137°
138°
139°
140°
141°

II

thesC4784
Superplasticity in an aluminum-zinc allo
3 2768 002 10419 2
DUDLEY KNOX LIBRARY